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## REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

BY F. W. CLARKE.

Received November 22, 1902.

IN the year 1900 an international committee on atomic weights was organized, composed of more than fifty representatives from chemical and other societies. Its conferences were necessarily conducted by correspondence, and the delays and difficulties of the work proved to be both serious and annoying. Accordingly, the committee, by vote, designated a smaller body of three representatives, and the latter now has the honor to report its recommendations.

On the fundamental question of standards, definite and formal action seems to be impracticable. By the original committee of the German Chemical Society the oxygen standard was adopted, but that proposal, while receiving strong support, also met with serious opposition. In fact, opinion, as expressed by individual voices, seems to be somewhat evenly divided upon this question, and around it there has already grown up a controversial literature of formidable proportions. To force the adoption of either standard, oxygen or hydrogen, appears therefore to be impossible, and for some time to come both are likely to be employed. Between them, experience must be the final arbiter. That standard

which best serves to coördinate chemical and physical knowledge will ultimately be chosen, and the other will gradually fall into disuse. Meanwhile, it is important that the most probable values for the several atomic weights should be indicated, and that every table of them should be consistent within itself. Such a table has been prepared by our distinguished predecessors, and its revision, as knowledge advances, seems to be our proper function.

In order that our work may be of the most general service, we have prepared a table in which both standards of atomic weight are represented. In most of its details it is identical with the table which was reported by the previous committee at the beginning of the year 1902.<sup>1</sup> Some changes, however, have in our judgment become necessary, and these may be briefly indicated as follows: when  $O = 16$ .

*Antimony.* In the former reports of the Committee, the value derived by Cooke from analyses of the bromide,  $Sb = 120$ , was adopted. This, however, ignores the work of Cooke and of Schneider upon antimony trisulphide, and the still more recent determinations made by Friend and Smith. The true number being therefore in doubt, we recommend the use of an average value, and put  $Sb = 120.2$ .

*Germanium.* The number 72.5 is more nearly in accord with Winkler's determinations than the former number 72.

*Hydrogen.* In the column which represents the oxygen standard, hydrogen has heretofore been assigned the value 1.01. The number 1.008 is, however, much more exact, and the error in 1.01 is too large to be perpetuated. Each figure should be given to the nearest *significant* decimal.

*Lanthanum.* During 1902 two new determinations of the atomic weight of lanthanum were published. According to Jones,  $La = 138.77$ . Brauner and Pavlicek found  $La = 139.04$ . Both investigations were conducted with great skill and care, and each one seems to have some points of advantage over the other. The average,  $La = 138.9$ , appears to be the safest value to adopt. These data naturally influence our judgment in the case of cerium, and we retain the Brauner number,  $Ce = 140$ , rather than adopt the lower estimates made by other observers.

*Mercury.* Taking into account all of the determinations which

<sup>1</sup> In No. 1 of the *Berichte*, for 1902.



have appeared, and giving great weight to the most recent measurements by Hardin, we regard the value  $Hg = 200$  as best warranted by the existing evidence.

*Palladium.* The atomic weight of this metal is in doubt. The best determinations give values ranging from 106 to 107. The mean between them,  $Pd = 106.5$ , has been provisionally adopted.

*Radium.* This element appears in the table for the first time. Madame Curie's determination of the atomic weight,  $Rd = 225$ , is probably not far from the truth.

*Selenium.* Judging from the work of Lenher, and the very recent determinations by Meyer, the former value,  $Se = 79.1$ , is probably too low. In order to give due weight to the newer measurements we write  $Se = 79.2$ .

*Tin.* The determinations by Bongartz and Classen, which seem to be the best, make  $Sn = 119$ . The former value, 118.5, is almost certainly too low.

*Uranium.* According to the very recent investigation by Richards and Merigold,  $U = 238.5$ .

*Zirconium.* The figure  $Zr = 90.6$  is apparently the most probable.

In thus assuming the duties assigned to us by the larger International Commission, we act upon the conviction that the purpose of our appointment is to secure the promptness and efficiency which is only possible with a comparatively small working body. In order to carry out this purpose, we must depend upon the coöperation and assistance of our colleagues. We therefore beg that they, and all other chemists who are interested in researches upon atomic weights, will aid us with their criticisms and advice. We especially ask that publications upon the subject shall be sent to us, in triplicate if possible, so that no matter of importance may be overlooked. Without support of this kind our work cannot be made fully effective.

The complete table of atomic weights, with the foregoing changes incorporated, follows:

F. W. CLARKE,  
T. E. THORPE,  
KARL SEUBERT,  
Committee.

1903.

## INTERNATIONAL ATOMIC WEIGHTS.

		O = 16.	H = 1.
Aluminum.....	Al	27.1	26.9
Antimony.....	Sb	120.2	119.3
Argon.....	A	39.9	39.6
Arsenic.....	As	75.0	74.4
Barium.....	Ba	137.4	136.4
Bismuth.....	Bi	208.5	206.9
Boron.....	B	11.	10.9
Bromine.....	Br	79.96	79.36
Cadmium.....	Cd	112.4	111.6
Caesium.....	Cs	133.	132.
Calcium.....	Ca	40.1	39.8
Carbon.....	C	12.00	11.91
Cerium.....	Ce	140.	139.
Chlorine.....	Cl	35.45	35.18
Chromium.....	Cr	52.1	51.7
Cobalt.....	Co	59.0	58.56
Columbium....	Cb	94.	93.3
Copper.....	Cu	63.6	63.1
Erbium.....	Er	166.	164.8
Fluorine.....	F	19.	18.9
Gadolinium....	Gd	156.	155.
Gallium.....	Ga	70.	69.5
Germanium....	Ge	72.5	71.9
Glucinum.....	Gl	9.1	9.03
Gold.....	Au	197.2	195.7
Helium.....	He	4.	4.
Hydrogen.....	H	1.008	1.000
Indium.....	In	114.	113.1
Iodine.....	I	126.85	125.90
Iridium.....	Ir	193.0	191.5
Iron.....	Fe	55.9	55.5
Krypton.....	Kr	81.8	81.2
Lanthanum....	La	138.9	137.9
Lead.....	Pb	206.9	205.35
Lithium.....	Li	7.03	6.98
Magnesium....	Mg	24.36	24.18
Manganese....	Mn	55.0	54.6
Mercury.....	Hg	200.0	198.5
Molybdenum..	Mo	96.0	95.3
Neodymium...	Nd	143.6	142.5
Neon.....	Ne	20.	19.9
Nickel.....	Ni	58.7	58.3
Nitrogen.....	N	14.04	13.93

		O = 16.	H = 1.
Osmium .....	Os	191.	189.6
Oxygen .....	O	16.00	15.88
Palladium .....	Pd	106.5	105.7
Phosphorus ....	P	31.0	30.77
Platinum .....	Pt	194.8	193.3
Potassium .....	K	39.15	38.86
Praseodymium .	Pr	140.5	139.4
Radium .....	Rd	225.	223.3
Rhodium .....	Rh	103.0	102.2
Rubidium .....	Rb	85.4	84.8
Ruthenium ....	Ru	101.7	100.9
Samarium .....	Sm	150.	148.9
Scandium .....	Sc	44.1	43.8
Selenium .....	Se	79.2	78.6
Silicon .....	Si	28.4	28.2
Silver .....	Ag	107.93	107.12
Sodium .....	Na	23.05	22.88
Strontium .....	Sr	87.6	86.94
Sulphur .....	S	32.06	31.83
Tantalum .....	Ta	183.	181.6
Tellurium .....	Te	127.6	126.6
Terbium .....	Tb	160.	158.8
Thallium .....	Tl	204.1	202.6
Thorium .....	Th	232.5	230.8
Thulium .....	Tm	171.	169.7
Tin .....	Sn	119.0	118.1
Titanium .....	Ti	48.1	47.7
Tungsten .....	W	184.	182.6
Uranium .....	U	238.5	236.7
Vanadium .....	V	51.2	50.8
Xenon .....	Xe	128.	127.
Ytterbium .....	Yb	173.0	171.7
Yttrium .....	Yt	89.0	88.3
Zinc .....	Zn	65.4	64.9
Zirconium .....	Zr	90.6	89.9

[CONTRIBUTIONS FROM THE LABORATORY OF THE PENNSYLVANIA STATE  
COLLEGE AGRICULTURAL EXPERIMENT STATION.]

### VIII. SOME CUBAN SOILS OF CHEMICAL INTEREST.

BY WM. FREAR AND C. P. BEISTLE.

Received October 18, 1908.

SOME time since, the writer received from Mr. Luis Marx, a Cuban tobacco grower, samples of a deep red soil from the

plantations San Antonio and Zorilla, in the municipality of Alquizar, in the southwestern part of the province of Havana. The results of the physical and chemical examination of these soils made by Mr. C. P. Beistle, under the direction of the writer, exhibit some peculiarities worthy of notice.

These soils were described as nearly virgin, deep and only slightly stony, and of a calcareous clay nature. The land lies high, is level, very permeable and never shows excess of standing water. The land is highly fertile, producing large crops of fine-leaved, elastic tobacco, numerous grasses and palms.

Dr. C. W. Hayes, of the United States Geological Survey, who recently made a reconnoissance of Cuba, states, in a letter to the writer, that the soils of the southern part of the province of Havana have a deep red color, and lie upon a horizontal or very gently undulating plain of subaerial denudation. No true coral reef rock has been noted in this part of the province, the larger part, probably, of the soil of this district being derived from a soft, friable chalk or chalky marl, though part of the limestone is a hard rock, projecting in angular points and weathered into a cavernous surface. The geological age of these rocks is not definitely ascertained; they are of a tertiary formation, probably corresponding to the Oligocene of the United States.

The soils considered in this paper have received no manurial application. The "surface" soils represent the upper twelve inches; the depth represented by the "subsoils" is not stated. The samples had been carefully sifted to remove coarse particles, before shipment.

#### SPECIFIC GRAVITY.

The specific gravity was determined by the usual pycnometric method, with results as follows:

	Specific gravity, 15.6° C.
San Antonio :	15.6° C.
Surface soil.....	2.677
Subsoil .....	2.681
Zorilla :	
Surface soil.....	2.714
Subsoil .....	2.711

The large amount of iron present is sufficient to account for

the rather high specific gravity. That there is little difference between the so-called surface and subsoils, is in accord with the fact that they are of similar color.

#### MECHANICAL ANALYSIS.

The subsoils were subjected to mechanical analysis by the Osborne beaker method, a tap-water of very slight alkalinity being used.

	San Antonio. Per cent.	Zorilla. Per cent.
Gravel (2-1 mm.) .....	....	....
Coarse sand (1-0.5 mm.).....	1.23	10.78
Medium sand (0.5-0.25 mm.) .....	13.63	12.75
Fine sand (0.25-0.1 mm.).....	32.80	30.84
Very fine sand (0.1-0.05 mm.) .....		
Silt (0.05-0.01 mm.).....	17.79	13.69
Fine silt (0.01-0.005 mm.) .....	15.10	12.72
Clay (less than 0.005 mm.).....		
Loss upon ignition (organic matter, combined water, etc.) .....	19.45	19.22
	100.00	100.00

About five-eighths of the water-free soil (residue from ignition) belongs to the group of 'sand,' while the 'clay' constitutes less, probably, than one-eighth of the whole.

This state of subdivision should produce the permeable texture and ready drainage said to mark the soils in place.

While these figures well represent the present condition of these soils, the use of a deflocculating agent like the 4 per cent. ammonia water used for the determination of 'active humus' or *matière noire* led to a complete breaking down of the 'sandy' particles into the finest clay. So fine were these particles that 70 per cent. or upwards of the mineral matter in the several soils passed through double parchment filters and a clear filtrate was obtained only by use of a Pasteur filter. The apparently sandy or loamy condition of these soils at the present time is doubtless attributable to the flocculant action of the carbonates of lime and magnesia present.

#### CHEMICAL ANALYSIS.

The soils were analyzed by the methods of the Association of Official Agricultural Chemists, the acid solution being, however,

subjected to a greater number of evaporations and re-extractions to assure the complete removal of silica therefrom. The means of closely concordant, duplicate determinations are given in the following table:

CHEMICAL ANALYSES OF CUBAN SOILS.

	San Antonio. Surface. Per cent.	San Antonio. Subsoil. Per cent.	Zo- rilla. Surface. Per cent.	Zo- rilla. Subsoil. Per cent.
Moisture (loss at 100° C. in water-oven)....	1.42	2.58	0.57	0.81
(Composition of water-free soils.)				
Acid insoluble (not decomposed).....	7.420	15.910	15.930	13.050
Soluble silica (dissolved by Na <sub>2</sub> CO <sub>3</sub> solution)	27.080	19.820	17.450	19.690
Potash .....	0.190	0.110	0.165	0.155
Soda .....	0.140	0.135	0.220	0.210
Lime .....	0.270	0.370	0.350	0.370
Magnesia .....	0.190	0.140	0.210	0.130
Mangano-manganic oxide.....	0.118	0.086	0.070	0.081
Ferric oxide .....	16.630	15.750	17.150	17.490
Alumina.....	27.860	29.350	28.255	29.270
Phosphoric acid.....	0.555	0.470	0.475	0.440
Sulphuric acid .....	0.035	0.065	0.060	0.030
Carbonic acid.....	0.555	0.315	0.275	0.305
Chlorine.....	trace	trace	trace	0.000
Loss on ignition, corrected for CO <sub>2</sub> expelled	18.912	16.808	19.566	18.930
	99.955	99.329	100.176	100.151
Phosphoric acid soluble in citric acid (1 per cent) .....	0.0087	0.0065	0.0060	0.0055
Potash soluble in citric acid (1 per cent.) ..	0.0098	0.0104	0.0125	0.0094
Nitrogen.....	0.255	0.145	0.230	0.165
Organic carbon.....	2.502	1.349	2.802	2.091
Organic matter corresponding (C × 1.724).	4.313	2.326	4.831	3.605
Water of combination :				
(a) Loss on ignition (corrected), less hygroscopic moisture and organic matter .....	14.599	14.482	14.735	15.325
(b) Total water obtained by combustion, less hygroscopic moisture and water derived from organic matter (assumed to contain 5 per cent. of hydrogen).....	15.249	15.331	14.484	13.723

Organic matter was determined by the method described by Van Bemmelen,<sup>1</sup> except that the hygroscopic moisture was de-

<sup>1</sup> *Landw. Versuchs-Sta.*, 37, 279.

terminated by the official method, instead of by drying *in vacuo* over sulphuric acid, as Van Bemmelen prefers.

The surface soils are distinctly richer in organic matter than the subsoils. There are not a very large number of recent analyses by this method on record for comparison. Van Bemmelen<sup>1</sup> found 2.65 to 5.07 per cent. in certain clay soils of Java and Sumatra. Warrington and Peake<sup>2</sup> found as much as 6.12 per cent. in an old pasture and as little as 0.65 per cent. in a clay subsoil. E. H. Hess,<sup>3</sup> working under direction of the writer, found in the limestone clay lands of the Pennsylvania Experiment Station, from 2.53 to 3.09 per cent. according to their manurial treatment. These few data warrant the opinion, however, that these virgin Cuban soils contain rather more humus than the more worn clay lands of the humid region contain.

Owing to the impossibility of eliminating the water of combination of the large amount of mineral matter associated with the active humus in its ammoniacal solution, the separate determination of this part of the organic substance was given up.

The soils contain very little sulphur and chlorine and probably little ferrous iron. It may therefore be assumed that the loss upon ignition of the "water-free" soil represents quite accurately the result of destruction of the organic matter and the expulsion of water combined with the organic materials and the hydrous minerals. The combined water has been estimated by direct subtraction of the computed organic matter from the total loss upon ignition. A check computation has been made, based upon the total moisture obtained upon combustion, corrected for hygroscopic moisture; from this total, there was subtracted the water corresponding to the hydrogen of the organic matter, which was assumed, after Van Bemmelen,<sup>4</sup> to contain 5 per cent. of this element. The results by the two methods differ beyond the limits of analytical error, thus failing to exhibit the surprising agreement that Van Bemmelen obtained in a variety of soils upon application of these methods.

The foregoing data are of especial interest in considering these soils as the products of certain geological processes. From this

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Cited by Wiley, "Principles and Practice of Agricultural Analysis," Vol. I, p. 323.

<sup>3</sup> Proc. Soc. Prom. Agr. Science, 1900.

<sup>4</sup> *Loc. cit.*

point of view the extensive decomposition effected by the action of hot hydrochloric acid is especially significant. It is emphasized by the following tabular statement:

	San Antonio.		Zorilla.	
	Surface. Per cent.	Subsoil. Per cent.	Surface. Per cent.	Subsoil. Per cent.
Undecomposed mineral matter, insoluble in HCl and Na <sub>2</sub> CO <sub>3</sub> solution...	7.420	15.910	15.930	13.050
Decomposed mineral matter:				
Gelatinous silica...	27.080	19.820	17.450	19.690
Dissolved in HCl.	46.088	46.476	46.955	48.176
Carbon dioxide...	0.555	0.315	0.275	0.305
Water of combination (α).....	14.599	14.482	14.735	15.325
	88.222	81.093	79.415	83.496
Organic matter.....	4.313	2.326	4.831	3.605
	99.955	99.329	100.176	100.151

The high solubility observed, is clearly not due, as in highly calcareous soils, to the presence of large quantities of calcite, magnesite or gypsum. It appears to be partially explained by the large amounts of iron oxide<sup>1</sup> and possibly, by those of alumina present; closer consideration of the facts compels the rejection of this explanation; for the iron oxide and alumina constitute only about 36 and 60 per cent. respectively of the acid-soluble material, while Hilgard<sup>2</sup> found that they constitute about 42 and 52 per cent. respectively of the average acid-soluble material in 466 soils, chiefly of the Gulf States in which the tertiary formation occurs.

Nor can the extensive decomposition be attributed to solvent action upon such anhydrous silicates as chrysolite, leucite, labradorite, epidote, phlogopite or biotite, which are capable of complete or quite extensive decomposition by the hot acid employed; the quantities of alkalis and magnesia dissolved, are too small to account for any large percentage of such minerals.

One indicative feature of these soils is the large proportion of soluble silica they yield upon decomposition, ranging from 17.45 to 27.08 per cent. The limestone clay of Lancaster County has

<sup>1</sup> Cf. Grouven, Soils of Benkendorf, Prerau and Tillada, *Jahrb. Agr. Chem.*, 10, 25.

<sup>2</sup> Bulletin 3, U. S. Weather Bureau, Division of Soils, p. 30.



been found to yield but 11.82 per cent.;<sup>1</sup> Maxwell,<sup>2</sup> analyzing a composite sample representing twenty soils from the Northern United States, chiefly of the humid region, obtained only 7.284 per cent.; Hilgard<sup>3</sup> found, in 119 soils from Tennessee, Mississippi, Louisiana, Indian Territory, and Texas, an average of 7.53 per cent., the accompanying insoluble matter being 74.74 per cent. Among the latter soils, however, thirteen show percentages of soluble silica ranging from 15.41 to 23.45 per cent., with accompanying insoluble matter, ranging from 34.8 to 53.19 per cent. The soluble silica in the Cuban soils is remarkable therefore for its large proportion to the entire soil, but not for exceptional quantity relative to the material decomposed by acid.

The large amount of water of hydration together with the ready decomposition of the soil under influence of hot acid, point to extensive weathering as the condition that has influenced the nature of the soil materials.

The results here observed may be due either to the slight resistance the original rock offered to weathering, to long exposure of more resistant rock, or to the separation of highly weathered material from that which has been less decomposed and its accumulation in the chalk beds from which these soils are derived.<sup>4</sup>

As instances of the first-class, the weathering of certain lavas may be cited. Maxwell<sup>5</sup> has found dark red, lava soils of Hawaii composed of readily decomposable hydrous silicates and iron oxide, the average of 120 analyses showing only 21.034 per cent. of resistant mineral matter, 16.168 per cent. of soluble silica, 17.499 per cent. loss upon ignition due chiefly to water of hydration, and 22.942 and 16.831 per cent. respectively of iron oxide and alumina soluble in acid. Hiola<sup>6</sup> and King<sup>7</sup> have reported analyses of tufa subsoils from Kumaba and Shimosa, Japan, that are marked by great loss upon ignition, high soluble

<sup>1</sup> Report Pennsylvania Experiment Station, 1894, p. 160.

<sup>2</sup> "Lava and Soils of the Hawaiian Islands," (1898), p. 101.

<sup>3</sup> X. Census, Vol. V.

<sup>4</sup> The tendency of lime to aid in forming zeolitic minerals from more resistant materials, can not be accepted in explanation of the observed ease of decomposition in these soils, because limestone clays in general are far more resistant to the action of acids.

<sup>5</sup> "Lavas and Soils of the Hawaiian Islands," (1898), p. 97.

<sup>6</sup> *Mitth. deutsch. Ges. Naturw. Volkerkunde Ostaustralien*, 1881: *Jahrb. Agr. Chem.*, 24, 25.

<sup>7</sup> *Jahrb. Agr. Chem.*, 24, 22.

silica and very low acid-resistant substance, though in these soils, the alumina greatly exceeds the iron oxide. Not all volcanic soils show these characters, those of Sumatra and Java<sup>1</sup> being quite different.

The second hypothesis requires the parent rock to have been highly homogeneous and to have weathered under conditions that protect the weathered products from mechanical separation. The range in state of weathering exhibited by the several mineral materials of most sedimentary soils, raises grave doubt as to the occurrence anywhere of conditions that would permit the removal of calcareous materials, such as these soils have experienced, without the removal, at the same time, of the finer, more highly weathered siliceous materials from those less weathered.

On the other hand, very fine silt and clay representing the most highly weathered portions of rocks and soils separated mechanically from the coarser materials, show marked similarity in composition to these Cuban soils. Merrill<sup>2</sup> found the silts from decomposed granite, gneiss and diabase to be marked by high water of combination (8-14 per cent.), and of gelatinous silica (12-23 per cent.), with a resistant residue ranging from 59 per cent. in the case of granite to 16 per cent. in that of diabase; the acid-soluble alumina ranged from 9.2 to 24.9 per cent. and in each instance exceeded the iron oxide. Loughridge<sup>3</sup> found, in the 21.64 per cent. of clay separated by mechanical analysis from a certain soil, conditions very different from those in the entire soil:

	Clay. Per cent.	Entire soil. Per cent.
Loss upon ignition.....	9.00	3.14
Acid-resistant mineral matter.....	15.96	70.53
Gelatinous silica.....	33.10	12.30
Acid-soluble material .....	58.06	14.66
	100.14	100.63

It would seem from these data last cited, that very fine silt carried far out into the gulf and deposited where the foraminiferous skeletons that form the chalk were accumulating, would give rise to a soil of the properties noted in these Cuban soils.

<sup>1</sup> Van Bemmelen, *Op. cit.*, 257 and 393.

<sup>2</sup> "Rocks and Rock-Weathering, and Soils," (1897), pp. 212-220.

<sup>3</sup> Proceedings A. A. S., 22, 81; Wiley: "Principles and Practice of Agricultural Analysis," Vol. I, p. 247.

These red soils are not of purely local occurrence. A. E. Woods<sup>1</sup> notes the prevalence in Bermuda of peculiarly deep red soils, whose color changes upon long cultivation. Earle<sup>2</sup> reports a partial analysis of a Cuban soil, of locality not stated, which exhibits high water of combination, low magnesia and alkalies, low acid-insoluble material (including gelatinous silica) but high calcium carbonate—a soil resembling those above reported except that it still retains much of the associated calcareous material. Watts<sup>3</sup> reports a red, limestone clay, tobacco soil from Mocho, Clarendon, Jamaica, that contains only 0.50 per cent. calcium carbonate, only 19 per cent. of acid-insoluble matter, including gelatinous silica, but which has 46 per cent. of iron and aluminum oxides and a large percentage of combined water.

While these soils may come under the Russian soil survey classification of laterites,<sup>4</sup> and like the true laterites of India possess deep red color, their large humus content differentiates them from the latter, from which they differ also in other respects.<sup>5</sup>

The peculiar violet-red color of these soils may be due to the dehydrating effect of salt water which W. Spring<sup>6</sup> and F. Katzer<sup>7</sup> have observed in case of uncombined ferric oxyhydrate deposited in delta-formations and upon sea-bottoms. Dr. Hayes, in the letter earlier mentioned, notes, however, that much of the soil apparently derived from the same formation in more easterly parts of Cuba, has a gray instead of red color. This difference may possibly be due to changes upon exposure of the virgin soil, such as Woods mentions as occurring in Bermuda.

The writer has found no record of any analysis of a soil of the Oligocene portion of the tertiary formation in the United States. Analyses of a few Eocene soils from the central prairie region of Mississippi reported by Hilgard<sup>8</sup> exhibit a very different composition.

<sup>1</sup> *Science*, June, 1902.

<sup>2</sup> Florida Experiment Station, Bulletin No. 19, p. 11.

<sup>3</sup> *Journal Jamaica Agricultural Society*, (1899), pp. 17-23; *Experiment Station Record*, No. 10, pp. 933-934.

<sup>4</sup> Cf. N. Sibirtzew, *Mem. pres. au. Congres. geol. Internat.*, St. Petersburg, 1897; *Jahrb. Agr. Chem.*, 42, 66.

<sup>5</sup> Cf. J. W. Leather: *Agr. Ledger*, (1898), No. 2, p. 83; *Experiment Station Record*, 10, 421.

<sup>6</sup> *N. Jahrb. Min.*, (1889), 1, 47; *Jahrb. Agr. Chem.*, 42, 49-50.

<sup>7</sup> Petermann's *geog. Mitth.*, 1897; *Jahrb. Agr. Chem.*, 42, 51.

<sup>8</sup> *X. Census*, Vol. V, p. 284.

## MINERAL CHARACTER.

Attempts at separation into groups of minerals of different specific gravity by the use of Thoulet's solutions of 3.09 and 2.7 sp. gr., and at identification of the minerals present by microscopic means, were rendered abortive by reason of the flocculation of the fine particles and their deep coloration by iron. The use of hydrochloric acid to remove the iron was not attempted because of the readiness with which the silicates present, are decomposed. The separate groups obtained by mechanical analysis each contained from 57 to 60 per cent. of iron and aluminum oxides, so homogeneous were the flocculation aggregates.

The proportions of the several chemical constituents present throw a little light upon the possibilities of combination. The low solubility of the potash and phosphoric acid in 1 per cent. citric acid indicates that the former is chiefly combined with silica and the latter with iron oxide or alumina; its quantity corresponds to 1.16 to 1.45 per cent. of ferric orthophosphate. The carbonic acid is sufficient in most cases to combine with nearly all of the alkaline earths, and, in case of the San Antonio surface soil, also with most of the alkalies; the existence of a little ferrous carbonate seems probable; in like manner, the humus is probably sufficient to combine with most of the alkaline and earthy bases, so that the carbonic and humus acids must exist in partial combination with the iron; owing to the low combining power of the humus, it would not tie up any large proportion of the latter element.

No analytical data were obtained to establish the degree of oxidation of the iron present, but the deep red color points to a highly oxidized condition. No iron-containing silicates remain in the acid-resistant material, which is colorless.

Concerning the nature of the siliceous compounds present: No large part of the gelatinous silica can be derived from zeolitic combination, as the small quantities of alkalies and lime, and the very slight loss of water that occurs when the air-dried soil is heated at a temperature of 100° C. show.<sup>1</sup> Assuming that such zeolites are present as natrolite or phillipite, which require a minimum of lime, they could not make up more than 4.5 per cent. of the dry soil nor yield more than 0.70 per cent. of gelatinous silica.

<sup>1</sup> Cf. Hillebrand: Bulletin No. 176, U. S. Geol. Survey, p. 36.

Assuming that the iron is present as ferric oxide chiefly, the small quantities of gelatinous silica and alumina required for zeolitic combination may be disregarded and their ratios be directly considered to ascertain what evidence they offer as to their compounds present. The silica-alumina ratios in these soils range from 1.029 to 1.636, chiefly approximating the latter figure. The average ratio for the 119 southern soils analyzed by Hilgard<sup>1</sup> is 1:0.71; those for the common aluminous minerals decomposable by hydrochloric acid with a liberation of gelatinous silica, range from 1:0.42 to 1:0.85; allophane and chloritoid (ratios 1:1.71 and 1:1.46 respectively) are the most prominent exceptions, but its dark color and low hydration exclude the latter from playing any important part, while allophane has a too low specific gravity and too high hydration. Upon any of the hypotheses as to the combination of the bases other than alumina, the average specific gravity of these remaining minerals must lie between 2.2 and 2.5 and the water of hydration between 14.6 and 17.0 per cent.

Hilgard<sup>2</sup> found, in the Eocene soil of Mississippi earlier cited, a ratio of 1:1.34, approaching that of these Cuban soils, and noted in many southern clays an excess of alumina. He suggests the presence of gibbsite, a hydrated alumina, as a means of explaining both the composition and the cultural peculiarities of these lands. Assuming the presence of a decomposable aluminum silicate with a silica-alumina ratio and hydration like those of kaolinite, approximately one-half of the alumina of the Zorilla surface soil would be left to be accounted for; but the great hydration of gibbsite (34.5 per cent.) excludes it from acceptance as the source of the alumina.

Schloesing<sup>3</sup> has employed a dilute solution of sodium hydroxide in recent studies upon the condition of alumina in French and Madagascar soils; kaolin and fatty clay gave up to this solvent an excess of silica over alumina and continued to do so upon repeated treatment; on the other hand, a certain ochreous type of Madagascar soils yielded from 1 to 2 per cent. of silica and 8 to nearly 12 per cent. of alumina in the first treatment, but an excess

<sup>1</sup> *Op. cit. supra.*

<sup>2</sup> *X. Census*, Vol. V, pp. 67 and 284.

<sup>3</sup> *Compt. Rend.*, 132, 1203; *Biol. Centrbl.*, 30, 723-730.

of silica on repeated treatment; this he regards as indicating the presence of free alumina which is dissolved at once by the alkali. That soil was gravelly, however, and much of the alumina was extracted from the coarser materials separated by mechanical analysis; the land was fertile. Owing to lack of material, it has been impossible to apply this treatment to the Cuban soils; many other interesting observations have been omitted for the same reason. It is hoped that the peculiarities of these widely extended West Indian soils here reported, may lead others to more thoroughly study them.

A few words respecting the fertility of these Cuban soils: Their present content of calcium and magnesium carbonates is sufficient to keep them permeable, to provide for nitrification and to furnish all of these elements that may be needed to keep the soil sweet and the plants well fed. Magnesia is less abundant than lime, a condition very commonly reversed in the soils of the Gulf States. Potash is low but, owing to the presence of the lime, may not exhibit deficiency for some time. Phosphoric acid is unusually abundant, but of low availability because of its combination with iron or aluminum. These lands will, for this reason, as well as to insure continuance of permeability, require occasional calcareous manuring. Nitrogen is present in liberal supply.

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[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE  
COLLEGE AGRICULTURAL EXPERIMENT STATION, No. 9.]

## THE EFFECTS OF FERMENTATION UPON THE COMPOSITION OF CIDER AND VINEGAR.

BY C. A. BROWNE, JR.

Received October 24, 1902.

THE present work comprises the results obtained in connection with an experiment begun at this Experiment Station in the Fall of 1898, which had for its object a chemical study of the cask methods of producing cider and vinegar, as ordinarily practiced in the rural sections of this country. So far as known, no experiments have been published thus far towards this end.<sup>1</sup>

### PLAN OF THE EXPERIMENT.

The juice for the experiment was prepared wholly from one

<sup>1</sup> Reference should be made to Bulletin No. 127, of the Va. Agr. Expt. Station, by W. B. Alwood and R. J. Davidson, entitled "Observations on the Production of Vinegar in Cellars," which has since come to the writer's attention.

kind of apples of an unknown variety. The apples were picked November 15, 1898, and were taken at once to a cider mill near-by where they were ground and pressed. A 25-gallon cask was filled with juice and then taken immediately to a cool, dry cellar, where it was kept throughout the experiment. The bung of the cask was loosely drawn to allow the escape of carbon dioxide during fermentation. The first sample for analysis was drawn the day after pressing. Samples were then drawn about every two weeks during the early stages of the alcoholic fermentation; afterwards during the latter part of the alcoholic fermentation and throughout the acetic fermentation, when chemical changes advanced less rapidly, analyses were made only monthly or bimonthly.

In sampling, a quart jar was usually filled, the cider being drawn off through a rubber siphon from about the middle of the cask. Care was taken not to disturb the sediment which settled out during the fermentation. The temperature of the cellar and cider were taken at the time of sampling, and the cask containing the cider was weighed occasionally in order to ascertain the losses from evaporation and seepage. The samples after taking to the laboratory were also weighed before beginning the analysis, to determine the amounts removed from the cask. The samples were drawn always in the morning, and the analytical work was begun immediately after taking to the laboratory to avoid vitiation of results due to the progress of the fermentation. If turbid or containing matter in suspension, the samples were filtered before analyzing. The results of the analytical work, covering a period of over three years, are presented in Table I.

#### THE ALCOHOLIC FERMENTATION.

The determinations of solids in Table I were unfortunately all made by the old method of drying at 100° C. in a water-bath. A constancy in weight could never be secured, and the percentages given represent simply the solid matter after ten to twelve hours' drying. As compared with a method<sup>1</sup> used later upon fruit products of drying *in vacuo* at 70° C., this procedure gives too low results, owing to the decomposition of levulose.

Looking at the percentages of the sugars, sucrose, dextrose, and levulose, in Table I, we notice during the first two weeks a

<sup>1</sup> This Journal, 23, 873.

TABLE I.—EFFECTS OF FERMENTATION UPON THE COMPOSITION OF CIDER AND VINEGAR.

Date of analysis.	Temperature of cellar.	Temperature of cider.	Weight of sample.	Weight of cider in can after empty- ing.	Specific gravity 17.5° C.	Solids at 100° C.	Ash.	Rotation, Ventiske, 400 mm. tube.	Levulose.		Dextrose.		Sucrose.		Total sugar after inversion.	Alcohol.		Volatile acid as acetic.		Fixed acid as ma- lic.		Pectin.	Water number.
									Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.	Per cent.	Per cent.				
Alcoholic fermentation.	1898, Nov. 16	44	49	2004	98070	1.0577	13.75	0.26	—44.18	7.38	2.90	2.93	13.36	0.43	0.04	0.42	0.12	...	...	...	...	...	...
	1898, Nov. 30	50	46	1017	.....	1.0462	12.25	0.24	—53.78	7.29	2.86	1.20	11.43	1.67	0.05	0.43	...	...	...	...	...	...	
	1898, Dec. 16	51	50	1000	.....	1.0331	9.48	0.24	—50.45	6.28	2.06	0.50	8.87	3.05	0.06	0.40	...	...	...	...	...	...	
	1899, Jan. 5	60	58	1033	.....	1.0133	5.92	0.24	—29.60	2.88	1.21	0.09	4.19	5.32	0.08	0.43	...	...	...	...	...	...	
	1899, Jan. 19	52	47	1050	.....	1.0067	4.53	0.24	—18.80	2.02	0.44	0.01	2.47	6.03	0.09	0.38	0.09	...	...	...	...	...	
	1899, Feb. 2	34	35	1062	.....	1.0026	3.03	0.25	—13.00	1.41	0.29	0.00	1.70	6.49	0.10	0.31	...	...	...	...	...	...	
	1899, Feb. 16	55	47	830	82440	1.0013	2.89	0.25	—11.06	1.17	0.21	...	1.38	6.70	0.11	0.30	...	...	...	...	...	...	
	1899, March 9	50	49	1045	80850	0.9982	2.24	0.25	—5.30	0.54	0.07	...	0.61	6.92	0.11	0.23	...	...	...	...	...	...	
	1899, April 3	47	45	1038	79040	0.9968	2.10	0.25	—3.40	0.30	0.00	...	0.30	6.93	0.17	0.21	...	...	...	...	...	...	
	1899, May 4	72	64	1941	76770	0.9969	1.94	...	—2.30	0.24	...	...	0.24	7.00	0.27	0.21	0.03	10.1	...	...	...	...	...
Acetic fermentation.	1899, July 27	67	62	1917	74960	0.9959	1.80	0.26	—1.50	0.11	...	...	...	6.86	0.52	0.20	...	...	...	...	...	...	...
	1899, Aug. 14	68	66	1060	.....	0.9965	1.53	0.26	—1.20	0.11	...	...	...	6.66	1.11	0.17	...	...	...	...	...	...	...
	1899, Oct. 2	55	50	1000	.....	0.9988	1.48	0.27	.....	...	...	...	...	6.01	1.77	...	...	...	...	...	...	...	...
	1899, Nov. 27	47	43	1079	.....	1.0017	1.42	0.26	.....	...	...	...	...	4.80	2.59	...	...	...	...	...	...	...	...
	1900, Feb. 14	54	46	1080	.....	1.0037	1.45	0.26	.....	...	...	...	...	4.54	3.67	...	...	...	...	...	...	...	...
	1900, April 20	65	58	1095	64980	1.0060	1.37	0.26	—1.40	0.18	...	...	...	3.77	4.31	0.14	...	...	...	...	...	...	...
	1900, July 31	70	66	1090	63620	1.0113	1.70	0.25	—1.20	0.22	...	...	...	2.61	5.98	...	...	...	...	...	...	...	...
	1902, Feb. 10	...	...	...	44570	1.0162	2.40	0.48	—5.00	1.20	...	...	...	0.00	3.33	0.06	...	...	...	...	...	...	...
	1902, March 9	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, April 7	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Destructive fermentation.	1902, May 19	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, June 16	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, July 22	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, Aug. 15	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, Oct. 13	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	1902, Oct. 13	...	...	...	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

1 All determinations, except that of solids, were made according to methods described in this journal, 23, 869 (1901).

<sup>1</sup> All determinations, except that of solids, were made according to methods described in this Journal, 23, 869 (1901).



rapid fall in the per cent. of sucrose, but that the percentages of dextrose and levulose remain nearly constant. This would indicate that in the beginning, by the action of the invertase upon the sucrose, the amounts of dextrose and levulose are restored nearly as fast as fermented. The following diagram will show the rates of decrease in the sugars, and their relations to alcohol and rotation more graphically.

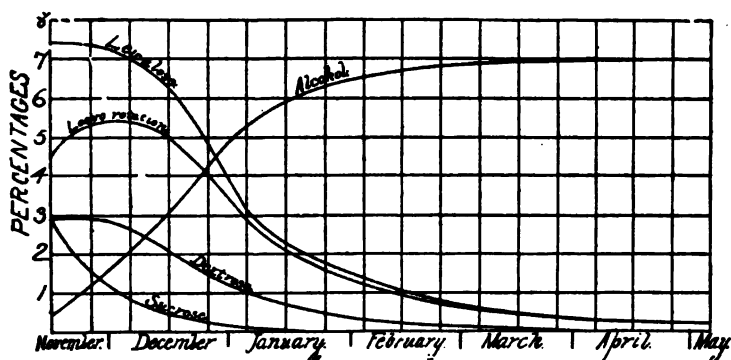


Diagram No. 1. Each division represents ten days.

The effect of the removal of the sucrose, which is strongly dextro-rotatory, is shown most strikingly by the marked rise at first in the levo-rotation; the maximum is soon reached, however, and the rotation then begins to fall, gradually at first,—the removal of sucrose and dextrose at this time very nearly counterbalancing the decrease in rotation that would be produced by the fermentation of levulose—, and then more suddenly owing to the increased rapidity in the fermentation of the levulose. The period of greatest chemical activity is from the fourth to the seventh week; we notice here the largest drop in the percentage of levulose, attended by the greatest rise in the percentage of alcohol. Another important fact is that while the sucrose and dextrose are completely removed by fermentation, a small amount of levulose remains unaffected. This is due to the formation of acetic acid, which arrests the alcoholic fermentation, as will be explained later. The levulose remains largely in excess of the dextrose during the whole fermentation, as is indicated by the marked levo-rotation at all times.

In plotting the curve for rotation one-tenth of the actual read-

ings given in Table I were used, in order to bring the curve within the range of the others. We note here that the rotation curve, as thus plotted, follows from its point of maximum the course of the levulose curve quite closely, gradually approaching the latter as the sucrose and dextrose diminish, until, with the elimination of these restraining factors the two curves merge, continuing afterwards together. The fact that the percentages of levulose, as calculated from the copper-reducing power, in the latter part of the alcoholic fermentation agreed so closely with one-tenth the observed polariscopic readings (Ventzke), in the 400 mm. tube, led the writer to calculate the theoretical Ventzke readings (20° C.) for a number of levulose solutions of different concentrations.

The formula<sup>1</sup> used was  $v = \frac{4WP}{34.68}$ , in which  $v$  = the Ventzke reading sought,  $W$  = grams of substance in 100 cc. solution, and  $P$  = the specific rotatory power at 20° C. for the given concentration. In calculating the value of  $P$  for levulose, the formula of Jungfleisch and Grimbert<sup>2</sup> was employed,  $[\alpha_D] = -[101.38 - 0.56t + 0.108(c - 10)]$ , in which  $t$  is the temperature of the solution and  $c$  the grams of levulose in 100 cc.

TABLE II.

Concentration. Levulose in 100 cc. Grams.	Calculated specific rotatory power. 20° C.	Calculated polariscopo- reading, Ventzke, 400 mm. 20° C.
10	— 90.18	— 104.00
5	— 89.64	— 51.69
2	— 89.33	— 20.60
1	— 89.21	— 10.26
0.5	— 89.15	— 5.14
0.2	— 89.12	— 2.06
0.1	— 89.11	— 1.02

Thus, for quantities of levulose up to 2 grams per 100 cc., one-tenth of the polariscopic reading in the 400 mm. tube at 20° C., gives a result agreeing within a few hundredths of the amount of levulose actually taken. This fact seems to offer a ready and easy means of determining levulose in the absence of other sugars. For low concentrations of levulose the differences between grams in 100 cc. and actual percentages are negligible. The close agree-

<sup>1</sup> This Journal, 23, 881.

<sup>2</sup> Landolt: "Das optische Drehungsvermögen," 2 Auflage, p. 524.

ment between the above calculated results and those actually observed in Table I affords not only a check upon the work, but also an indication that levulose is the only important optically active body in completely fermented ciders.

As regards other chemical changes produced during the period of alcoholic fermentation, we observe a slow, but gradual increase in the percentage of acetic acid, while as regards the percentage of fixed or malic acid, the reverse is true. Just how the malic acid is destroyed is not well understood. A similar diminution takes place with tartaric acid in the fermentation of grape juice. The amount of pectin or gummy matter precipitated by alcohol was determined in a few cases during the alcoholic fermentation, and also seems to undergo a decrease, due no doubt to sedimentation.

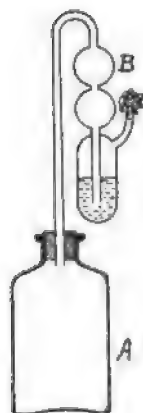
Determinations of the ester number, or cubic centimeters of N/10 sodium hydroxide necessary to saponify the esters distilled from 100 cc. of cider were made in the latter part of the period of alcoholic fermentation. The results seem to indicate an increase in the volatile esters up to the point of greatest alcohol content; with the development of acidity, however, as shown by later analyses, these esters seem to be partly broken up. The maximum ester number of 10.1 would be equivalent to 0.09 per cent. of ethyl acetate.

#### THE SUGAR-ALCOHOL RATIO.

Kulisch<sup>1</sup> in an experiment upon the fermentation of apple juice calculates that 100 parts of sugar after inversion yield 49.5 parts of alcohol, but does not state whether the experiment was conducted in a cask or bottle.<sup>2</sup> The results of Kulisch are based

<sup>1</sup> Kulisch: *Landw. Jahrb.* 19, 111, (1890).

<sup>2</sup> Larger yields of the alcohol are, of course, obtained where fermentation bottles are used since losses from evaporation are prevented. In some fermentation experiments carried out by the writer under the direction of Professor Alfred Koch, at the University of Göttingen, there were obtained in one experiment from 100 parts of sugar, 50.49 parts alcohol and 48.22 parts carbon dioxide. Sterilized grape juice and a pure yeast culture (Reinhefe No. 13) were employed, so that all injurious fermentative changes, acetic, etc. were excluded. The fermentations were carried out in flasks of the form shown in the accompanying figure. After sterilizing the apparatus the bottle *A*, holding about 500 cc., is filled about half full with a known quantity of the sterilized medium (must, cider, wine, etc.) and then, after inoculating, tightly closed with the ar-



upon the supposition that the volume of liquid remains constant throughout the fermentation; while this assumption is practically correct as is shown by the results of Stein<sup>1</sup> and others, it would not hold where there were losses from evaporation and seepage, as is always the case where the fermentation takes place in casks.

To determine the yield of alcohol from sugar in the experiment, the calculation was made as follows, using the data given in Table I.

Date.	Weight of cider. Grams.	Sugar in cider. Per cent.	Sugar in cider. Grams.	Alcohol in cider. Per cent.	Alcohol in cider. Grams.
Nov. 16	97070	13.36	12968.6	0.43	417.4
May 4	76770	0.24	184.2	7.00	5373.9
	12968.6 grams = total weight of sugar at beginning of fermentation.				
deduct	184.2	" = "	" " " " " " end	"	"
	12784.4				
deduct	585.6	grams = total weight of sugar removed by samples.			
	12198.8	grams = weight of sugar actually fermented.			
	5373.9	grams = total weight of alcohol at end of fermentation.			
deduct	417.4	" = "	" " " " " " beginning of fermenta-		[tion.
	4956.5				
add	579.0	grams = total weight of alcohol removed by samples.			
	5535.5	grams = weight of alcohol formed during period of fermenta-			
	5535.5	[tation.			
	12198.8	= 0.454, sugar-alcohol ratio.			

In other words 100 parts of sugar in the experiment gave an actual yield of 45.4 parts alcohol. This is 88.8 per cent. of the theoretical yield and about 90 per cent. of the best results of laboratory experiments.

The principal cause of this loss in alcohol is that from volatilization. A small laboratory experiment upon the effects of evaporation, at room temperature, on a dilute alcohol solution showed the following:

	Weight of solution. Grams.	Specific gravity. 15.5° C.	Alcohol. Per cent.	Alcohol in solution. Grams.
At beginning .....	188.5	0.98647	8.11	15.29
After forty-eight hours ..	142.2	0.99802	1.04	1.48
Loss .....	46.3	.....	....	13.81

rangement B. The bottom bulb is filled about half full with sulphuric acid (1:1), which seals the flask from without, but does not interfere with the escape of carbon dioxide. The mouth of the bulb is closed with a small wad of cotton. By weighing the apparatus from time to time and noting the loss in weight, one is enabled to follow the rate of fermentation very closely.

<sup>1</sup> *J. Soc. Chem. Ind.*, 19, 127-8 (1900).

Thus 30 per cent. of the loss on evaporation was due to alcohol, while of the total amount of alcohol originally present 90 per cent. disappeared by volatilization at room temperature. This illustration is, of course, an extreme case; the experiment was conducted in an open beaker and a relatively large surface (10 square inches) was exposed to evaporation in proportion to the amount of solution.

The loss from evaporation in the cider experiment during the 169 days of the alcoholic fermentation was calculated as follows:

	97070 grams = weight of cider at the beginning.
deduct	76770 grams = weight of cider at the end of the alcoholic fermentation.
	<hr/> 20300
deduct	12020 grams = weight of cider removed by samples.
	<hr/> 8280 grams = loss from evaporation and carbon dioxide.
deduct	5964 grams = theoretical weight of carbon dioxide by fermentation [of 12198.8 grams sugar.
	<hr/> 2316 grams = the calculated loss from evaporation and seepage.

The outer surface of the cider cask showed no signs of leakage, so that the greater part of this loss, which amounts to about 2.4 per cent. of the total amount of liquor, was probably due to evaporation,—this being increased no doubt by the abundant evolution of carbon dioxide early in the fermentation. In this loss from evaporation a considerable quantity of alcohol must have escaped.

Very serious losses of alcohol may result in cider-making, from the development of the acetic ferment. During the period of alcoholic fermentation in the experiment, there was formed 0.23 per cent. acetic acid, equivalent to about 0.2 per cent. alcohol; and sufficient to cause a decrease of 0.7 in the percentage of alcohol formed from sugar.

The average percentage of acetic acid in a number of ciders, obtained from farmers and analyzed at this station, was found to be 0.69, the results ranging from 0.24 to 1.96 per cent. Kulisch<sup>1</sup> found in the analysis of many German ciders an average of only 0.04 per cent. acetic acid, the range being from 0.01 to 0.14 per cent. This low degree of acidity is especially noteworthy and is an indication of the extreme care employed in the fermentation.

<sup>1</sup> Kulisch: *Landw. Jahrb.*, 19, 88 (1890).

By racking ciders off after the main fermentation into other casks and bunging tightly, a considerable part of the losses of alcohol from evaporation and acetification may be prevented, and a much better quality of cider obtained.

#### THE ACETIC FERMENTATION.

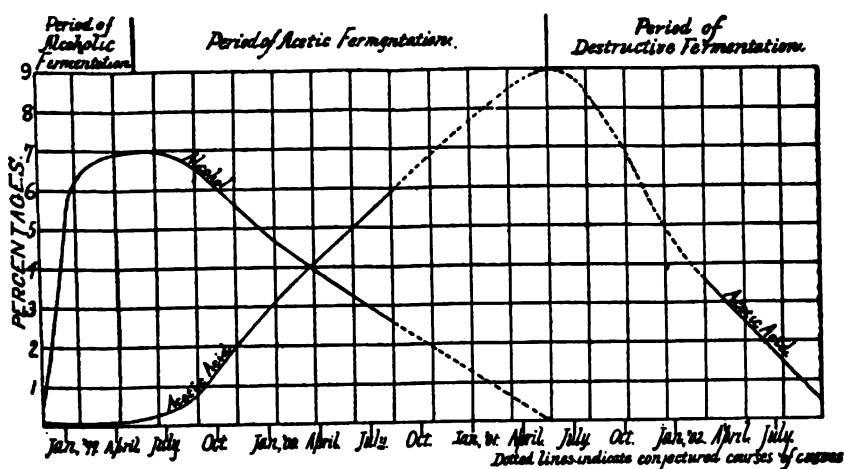
The cider obtained by the alcohol experiment was used for the experiment on acetification. The cider was not transferred; but to facilitate the process of oxidation the bung of the cask, which had been only loosely inserted during the alcoholic fermentation, was now removed entirely. The results of the analytical work are tabulated in the second part of Table I. The writer, owing to a temporary absence of eighteen months, was unable to carry the experiment through to the completion of acetification. The last analysis shows the presence of 2.61 per cent. alcohol and this would correspond to about 3 per cent. more acetic acid, so that the vinegar at the end of acetification showed probably about 9 per cent. acetic acid. The work was, however, carried far enough to illustrate the principal chemical changes of acetification and to establish an alcohol-acetic acid ratio.

Inspecting Table I we notice that with the progress of acetification the specific gravity, which had been steadily decreasing since the beginning of the alcohol fermentation, now begins to increase. The percentage of solids determined by drying at 100° C. undergoes a slight diminution; the last analysis, however, seems to show an increase, due, perhaps, to a concentration of the liquid from evaporation. Ash remains constant. The percentage of malic or fixed acid continues to decrease, as during the alcoholic fermentation. The percentage of levulose continues to decrease at first slightly,—the result of the last remaining efforts of the alcoholic ferment,—but upon the percentage of acetic acid reaching 0.5 undergoes no further diminution. The alcoholic fermentation proceeds best in the presence of a minimum amount of acetic acid. A percentage of 0.5 acetic acid will retard the alcoholic fermentation considerably, and experiments by Lafar<sup>1</sup> show that out of fifteen different varieties of yeasts only three were able to produce any fermentation at all when the

<sup>1</sup> Lafar: *Landw. Jahrb.*, 24, 445 (1895).

amount of acetic acid exceeded 1 per cent. Many farmers and vinegar manufacturers make a foolish practice of adding fresh apple-juice to old vinegar stock, in the hope of thus securing a more rapid conversion of the product into vinegar and then complain that their vinegar "won't make." The sugar of the juice must first undergo the alcoholic fermentation before the acetic fermentation can begin, and by adding apple-juice to old vinegar, the alcoholic fermentation may not only be checked, but even absolutely prevented. The writer knows of instances where such mixtures have remained for years without fermenting. This fact no doubt explains the high percentage of reducing sugars found occasionally in samples of cider vinegar.

The relation between alcohol and acetic acid in the fermentation experiment is illustrated graphically in the following diagram.



The process of acetification advances very slowly until about July when it receives a sudden start, probably through the influence of the warm summer temperature. The conjectured courses of the alcohol and acetic acid curves, for the time when no analyses were made, are indicated by dotted lines.

#### THE ALCOHOL-ACETIC ACID RATIO.

Calculations made from the specific-gravity tables of alcohol and acetic acid, indicate that there is a slight increase in volume

during the acetic fermentation, provided no loss occurs from evaporation. Assuming that the volume remains unchanged during the fermentation, a calculation of the ratio of alcohol to acetic acid, from the data in Table I, gives a value of 1.33, which instead of being lower is higher than the theoretical figure 1.30. This is to be explained by a concentration of the acetic acid, during the experiment, from evaporation. A laboratory experiment<sup>1</sup> upon the effects of evaporation on a dilute solution of acetic acid at room temperature showed the same effect.

	Weight of solution. Grams.	Specific gravity. 15.5° C.	Acetic acid by titration. Per cent.	Acetic acid in solution. Grams.
At beginning.....	188.5	1.01184	8.53	16.08
After forty-eight hours ..	155.5	1.01326	9.04	14.06
Loss .....	33.0	.....	....	2.02

This shows a concentration of the solution from evaporation, there being an increase of 0.5 per cent. acetic acid in forty-eight hours. A calculation, based upon the actual amounts of acetic acid in the solution, shows, however, a loss of 2.02 grams acetic acid from evaporation or 12.5 per cent of the original amount. Vinegars may, therefore, become stronger through evaporation, notwithstanding that there is an actual loss of acetic acid.

To determine the true ratio of alcohol to acetic acid in the experiment, the following calculation was made, using data from Table I.

	Date.	Weight of vinegar.	Alcohol in vinegar. Per cent.	Alcohol in vinegar. Grams.	Acetic acid in vinegar. Per cent.	Acetic acid in vinegar. Grams.
	1899, May 4	76770	7.00	5373.9	0.27	207.3
	1900, July 31	63620	2.61	1660.5	5.98	3804.5
	5373.9 grams = total weight of alcohol at beginning of experiment.					
deduct	1660.5	"	"	"	"	end of experiment.
	3713.4					
deduct	432.8	grams = weight of alcohol removed by samples.				
	3280.6	"	"	"	"	actually fermented.
	3804.5	grams = total weight of acetic acid at end of experiment.				
deduct	207.3	"	"	"	"	beginning of experi- [ment.
	3597.2					
add	219.4	grams = weight of acetic acid removed by samples.				
	3816.6	"	"	"	"	formed during period of ex- [periment.
	3816.6					
	3280.6	= 1.163, ratio of alcohol to acetic acid.				

<sup>1</sup> This experiment was conducted at the same time and under similar conditions as the experiment upon evaporation of alcohol in dilute solution, page 22.



In other words 100 parts of alcohol in the experiment gave an actual yield of 116.3 parts acetic acid, instead of 133.2 parts as calculated according to constant volumes. This yield is 89.2 per cent. of the theoretical. The greater part of this loss occurred no doubt from volatilization of both alcohol and acetic acid. In the experiment during the period of acetification the bung was withdrawn from the cask entirely, and considerable loss from evaporation might easily take place.

The loss from evaporation during the fifteen months of the acetification experiment was computed as follows.

	76770 grams = weight of vinegar at beginning of experiment.
deduct	63620 grams = weight of vinegar at end of experiment.
	<hr/> 13150 grams.
deduct	8321 grams = weight of vinegar removed by sample.
	<hr/> 4829 grams.
add	2296 grams = calculated weight of oxygen absorbed to oxidize
	[3280.6 grams alcohol.
	<hr/> 7125 grams = calculated loss from evaporation and seepage.

This loss or shrinkage is over 9 per cent. of the weight of cider at the end of the alcoholic fermentation, and if calculated to the completion of acetification would equal nearly 15 per cent.

Another source of loss of acetic acid, in addition to that from volatilization, occurs as a result of certain destructive fermentative changes. This will be spoken of more fully under the subject of deterioration of vinegar. The ratio of sugar to acetic acid in the experiment would be equal to the product of the sugar-alcohol and alcohol-acetic acid ratios,  $0.454 \times 1.163 = 0.528$ . That is, 100 parts of sugar produced 52.8 parts acetic acid, which is about 80 per cent. of the theoretical yield 66.6.

#### THE DETERIORATION OF VINEGAR.

It is a fact well known among vinegar manufacturers that vinegars after long standing deteriorate and lose their strength. Such vinegars they say become "overaged."

A good example of a deteriorated vinegar is afforded in the fermentation experiment. After an interval of eighteen months from the analysis on July 31, 1900, an examination of the vinegar was made with the results shown at the bottom of Table I. The vinegar, when drawn, contained a large amount of sediment,

mixed with mother and had to be filtered. There were also present many dead larvae of vinegar flies (*Drosophila*); whether these may have played any important part in the process of deterioration is uncertain.

Comparing the analytical results of the deteriorated vinegar with those of eighteen months before, we notice some very decided changes. The solids and ash have both undergone a marked increase, due to a concentration of the vinegar from evaporation. The bung-hole of the vinegar cask had remained open since the time of the former analysis and the weight of vinegar had decreased from 63 to 44 kilos, a loss of over 30 per cent. We note also in Table I that the alcohol has entirely disappeared in the deteriorated vinegar, as was to be expected, and that the percentage of malic acid, which had been decreasing from the very first, has fallen off to 0.06 per cent.

The acetic acid, it is noticed, has decreased over 2.5 per cent. since the last determination. The loss in acetic acid from deterioration is, however, much greater than this, as the process of acetification at the time of the former analysis was incomplete. Determinations of acidity in the deteriorated vinegar were made from month to month, and the decrease continued quite regularly, though somewhat faster in the summer months, at the rate of about 0.1 per cent. per week. This is also shown graphically in diagram No 2.

This marked decrease in the percentage of acetic acid is due mostly to a destructive fermentation. There are a number of acetic acid-consuming organisms, but of first importance among these are the acetifying bacteria themselves. It was first established by Pasteur that the acetic acid bacteria, after converting the alcohol into acetic acid, then consume the latter, forming carbon dioxide and water,  $\text{CH}_3\text{COOH} + 4\text{O} = 2\text{H}_2\text{O} + \text{CO}_2$ . The saying sometimes heard that vinegar on long standing "eats itself up" is therefore really true. This secondary action of the acetic ferment sets in no doubt before the complete acetification of the alcohol, and this would diminish somewhat the yield of acetic acid from alcohol.

#### THE NATURE OF THE ORGANISMS PRODUCING DETERIORATION.

A sample of the deteriorated vinegar poured off into a large

bottle continued to develop mother in large quantities, and the question arose as to the exact nature of the ferment producing the deterioration. A chemical examination of the mother, which was taken before the period of deterioration and of that found in the degenerated sample, showed that the organisms, which had produced acetification, and those causing the deterioration were of an entirely different nature, although both belonged to the class of acetic bacteria. Pieces of the mother from the deteriorated vinegar were boiled with successive portions of dilute sulphuric acid and soda, to remove incrusting substances, and then, after washing, treated with chloride of zinc and iodine; an intense blue coloration developed, characteristic of cellulose. The same reaction was also produced with sulphuric acid and iodine. This proves the ferment to be not the ordinary *mycoderma aceti* but *bacterium xylinum*<sup>1</sup> or an allied form,—the slimy envelopes of *mycoderma aceti* or *bacterium Pasteurianum* not containing cellulose. The presence of a cellulose-forming organism in the deteriorated vinegar is especially noteworthy, inasmuch as the mother taken from the vinegar before deterioration gave no cellulose reaction, showing that the ferment, which produced acetification, was of the ordinary *mycoderma* type. Bertrand<sup>2</sup> states that the small red vinegar flies (*Drosophila cellaris*), which frequent places where fruit juices, etc., are fermenting, inoculate the latter with the sorbose bacterium<sup>3</sup> (*bacterium xylinum*). As was before stated many larvae of vinegar flies were found in the deteriorated vinegar and we may have here a source of the organisms, which seem to have supplanted the original acetifying bacteria.

#### THE FORMATION OF REDUCING SUBSTANCES IN "OVERAGED" VINEGAR.

A singular fact in connection with the results upon deterioration is the high increase in the percentage of reducing sugar, which is also attended by a considerable increase in the levorotation. This cannot be explained altogether by the concentration of the vinegar from evaporation, since with a reduction in volume of only 30 per

<sup>1</sup> Lafar: *Technische Mykologie*, Bd. I, p. 346. The *Bacterium xylinum*, first studied by A. J. Brown, forms a very tough, thick mother, popularly designated in England as "vinegar plant."

<sup>2</sup> Bertrand: *Compt. Rend.*, 122, 900; Maquenne: "Les Sucres," Paris, (1900), p. 581.

<sup>3</sup> The Sorbose bacterium and *Bacterium xylinum*, at first considered different, have been proved by Emerling to be identical. *Ber. d. chem. Ges.*, 32, 541.

cent., we observe that the percentage of sugar, calculated as levulose, has increased to over five times its original amount. The percentage of sugar as levulose no longer agrees with one-tenth the rotation Ventzke in the 400 mm. tube, as was the case early in the process of acetification, but is over twice the same, so that other reducing substances besides levulose must be present,—the result no doubt of certain fermentative changes. This latter assumption does not seem improbable, when we consider the fact that the solids of vinegar are made up to a great extent of glycerol, pectin, and other substances, probably of a carbohydrate nature, and hence easily subject to chemical transformation.

To ascertain more fully the nature of the reducing bodies in the deteriorated vinegar, a quantity of the sample, after filtering from the mother, was treated with a solution of phenylhydrazine dissolved in acetic acid. After heating for twenty minutes on the steam-bath, a flocculent precipitate began to form and, on cooling, a thick yellowish colored magma was obtained. This was filtered off, and by fractional crystallization from alcohol was found to contain two well-defined osazones.

Osazone No. 1, present in considerable amounts, was easily soluble in alcohol, but less soluble in water. After recrystallizing several times from dilute alcohol, a yellowish colored product was obtained melting at  $142^{\circ}$ - $143^{\circ}$ . The compound turned slightly brown on long exposure to the air and light.

Osazone No. 2, present in only small amounts, was almost insoluble in alcohol and very difficultly soluble in ether. Its quantity was so small that no attempt was made to recrystallize it. It was purified by washing with small amounts of alcohol and ether. The compound consisted of a pale yellow crystalline powder, melting at  $240^{\circ}$ - $242^{\circ}$ .

An elementary analysis of osazone No. 1 showed it to have the composition of a phenyl hexosazone.

	Found. Osazone No. 1. Per cent.	Calculated. Phenylhexosazone, $C_{18}H_{20}N_4O_6$ . Per cent.
Carbon .....	60.45	60.27
Hydrogen .....	6.22	6.20

Of the some twelve known isomeric phenylhexosazones only one has a melting-point agreeing with that of osazone No. 1 and

that is the phenylformosazone, described by Fischer,<sup>1</sup> melting at  $-144^{\circ}$ . Formose,<sup>2</sup> a body of great interest in the synthesis of sugars, has not been found hitherto in any natural product. It has been prepared synthetically by the condensation of formaldehyde in alkaline solution. In this condensation a mixture of substances is formed, but the name formose is applied by Fischer only to the compound giving the above osazone. The arrangement in composition and melting-point of osazone No. 1 with phenylformosazone, while not an absolute proof of the identity of the two compounds, yet furnishes an indication of the presence in the deteriorated vinegar either of formose or of some unknown hexose sugar.

An elementary analysis of osazone No. 2 showed that it was not an osazone of any of the sugars. Its composition agrees, however, with that of phenyldiacetylosazone.

	Found. Osazone No. 2. Per cent.	Calculated. Phenyldiacetyl- osazone, $C_{16}H_{16}N_4$ . Per cent.
Carbon .....	71.90	72.10
Hydrogen .....	7.08	6.82

Diacetylosazone, first prepared by Pechmann,<sup>3</sup> is described as a yellowish colored, finely crystalline compound, melting at  $245^{\circ}$ , almost insoluble in alcohol or water, and difficultly soluble in ether. These properties agree exactly with those of osazone No. 2. This osazone can be formed either from diacetyl,  $CH_3COCOCH_3$ , or from dimethyl ketol,  $CH_3-CHOH-CO-CH_3$ . The latter compound being a ketone, alcohol is closely allied to the sugars and, as described by Pechmann,<sup>4</sup> reduces Fehling's solution strongly, even in the cold.

The separation of the two osazones just described from the deteriorated vinegar goes to confirm, what was previously surmised from the changes in reducing power and rotation, *viz.*, that other reducing substances besides levulose must be present as a consequence of fermentative changes. As a matter of fact, the levulose seems to have disappeared completely, since no traces of other osazones besides the two mentioned could be found.

As a remedy against deterioration, vinegars intended for storage should be racked off into clean casks, the latter filled full

<sup>1</sup> Fischer: *Ber. d. chem. Ges.*, 21, 989-991.

<sup>2</sup> See Tollens: "Die Kohlenhydrate," Bd. II, p. 39 and p. 135; also Maquenne: "Le Sacres," p. 398.

<sup>3</sup> Pechmann: *Ber. d. chem. Ges.*, 21, 2754.

<sup>4</sup> Pechmann: *Ibid.*, 22, 2214.

and tightly bunged. Since none of the acetic organisms can thrive without air, their further development is thus prevented, and the loss from destructive fermentation reduced to a minimum.

#### MISCELLANEOUS RESULTS.

In the following tables a few miscellaneous results are given, which may have a certain interest, though not bearing directly upon the main part of the fermentation experiment.

*The Composition of Vinegar Settlings.* During the alcoholic and acetic fermentation a large quantity of matter settles to the bottom of the cask. A quantity of this material, as obtained from the cask at the close of the fermentation experiment, was filtered off, washed, and submitted to an examination.

The material, which was of a brownish color, was seen under the microscope to consist largely of dead yeast cells; fragments of mother, particles of pomace, and amorphous flocks of a pectinous character were also observed. In addition to these was noted a number of spherical bodies, more or less marked with a linear depression, which were stained blue with iodine. Measurements showed these to range in size from 0.004 mm. to 0.016 mm., which thus identifies them with the starch granules of the apple.<sup>1</sup> This starch, which was removed from the apple at the time of pressing the cider, settles out and remains unaffected by the fermentation.

An analysis of the dried settlings showed them to have the following composition:

TABLE III.

	Per cent.
Moisture.....	4.91
Fat.....	1.69
Protein.....	20.13
Ash.....	2.65
Crude fiber.....	5.69
Nitrogen-free extract.....	64.93

A determination of pentosans showed only 1.48 per cent., so that the high percentage of nitrogen-free extract remains unaccounted for. The amounts of starch and pectin present were not determined, and these no doubt would make up a considerable part of the deficiency.

*Composition of Ash.*—Analyses were made of the ash from the apples and cider used for the fermentation experiment and of the ash from the settlings, taken from the cask after closing the experiment.

<sup>1</sup> Bulletin No. 58, Pennsylvania Department of Agriculture, p. 12.

TABLE IV.

	Ash of apples. Per cent.	Ash of cider. Per cent.	Ash of settlings. Per cent.
K <sub>2</sub> O.....	58.31	60.60	19.94
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	12.26	6.00	19.97
CaO.....	undetermined.	1.15	4.17
MgO.....	undetermined.	undetermined.	2.22
P <sub>2</sub> O <sub>5</sub> .....	12.51	7.12	25.64
SO <sub>3</sub> .....	6.87	4.15	0.14
SiO <sub>2</sub> .....	1.65	1.90	24.23
Undetermined CO <sub>2</sub> , etc	8.40	19.08	....

The high percentage of silica and phosphoric acid in the ash of the settlings is noteworthy; no carbonates were present.

In concluding, the writer expresses acknowledgment to Messrs. C. P. Beistle and A. N. Diehl, former assistants at this experiment station, for help in much of the analytical work of the foregoing experiments, and also to Dr. William Frear for his encouragement and many kindly suggestions, and under whose initiative the work was first begun. The writer owes an especial debt of gratitude to his former teacher, Professor Alfred Koch, of Göttingen University, for much valuable advice and information upon this subject of fermentation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS.]

## A CONTRIBUTION TO THE CHEMISTRY OF FATIGUE.

BY HENRY WINSTON HARPER AND MARGARET HOLLIDAY.

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### INTRODUCTION.

SOME years since, while engaged in the study of the phenomena of fatigue and breathlessness, the senior author of this contribution was struck with an apparent resemblance to the phenomena encountered when caffeine is administered in toxic doses. It seemed clear that the phenomena of fatigue were largely due to the action of a chemical substance present in toxic quantity in the blood-stream, and that this substance had its origin in the muscles, *i. e.*, that the metabolism within the muscles undergoing excessive exercise was accompanied with a production of incompletely

oxidized chemical complexes, that these complexes possessed toxic qualities, and, transported by the blood-stream throughout the body, gave rise to the phenomena grouped under fatigue. Fatigue then arises from autointoxication, but the toxic substances are not the simple end-products, urea, carbon dioxide, etc., but are far more complex bodies, among which may possibly be found one or more of the alkyl derivatives of xanthine. A preliminary investigation pointed to the presence of methyl derivatives of xanthine, and encouraged further prosecution of the inquiry; but multitudinous duties stopped the work before fruitful results were obtained. The research was not again entered upon until during the session of 1901-1902, when the present investigation was undertaken in conjunction with Miss Margaret Holliday.

It should be distinctly understood that the results here presented are not offered as a solution of the problem of fatigue, but the data thus far accumulated are of sufficient interest to justify publication, and they represent at least a modest contribution to the chemistry of the subject. The main problem will be further investigated.

Lombard<sup>1</sup> states that: "The working cell liberates energy at the expense of its store of nutriment and oxygen, and through oxidation processes forms waste-products which are poisonous to its protoplasm. The fatigue which results from functional activity has, therefore, a twofold cause, the decrease in energy-holding compounds available for work and the accumulation of poisonous waste-matters." A similar statement is made by other physiologists; but it will be seen that such statements are only broad generalizations, and when specific information concerning the nature of the waste-products and the chemistry of their formation and action is sought, it then becomes apparent that a very large field for chemical research needs to be more deeply explored. It is equally clear that this field of investigation is full of difficulties, and, therefore, presents opportunities for numerous investigators. Like all biochemical problems, it includes a large amount of virgin soil.

The main object of this particular research was to shed some light upon the chemical nature of the metabolites which gain access to the blood-current during excessive muscular exertion.

<sup>1</sup> Lombard: "An American Text-Book of Physiology," 1901, Vol. II, p. 70.



It was not expected that anything approaching a solution of the problem would be speedily gained, but a hope of progress was entertained, and a definite plan of work for the future has been evolved. The question of the production of the methyl derivatives of xanthine within the muscles at the time of excessive muscular exertion and their discharge into the blood-stream was especially investigated, and every precaution was taken to exclude the access of these bodies through extraneous sources. The results are presented upon their own merits. A fuller discussion will accompany a later investigation.

#### ANALYTICAL METHODS USED.

A great deal of time was devoted to the calibration of apparatus, and to the trial of the numerous analytical methods used in biochemical work with a view to ascertain the limits of accuracy and suitability for this particular inquiry. The usual numerous disappointments were encountered; and some of the methods finally adopted are far from being wholly satisfactory. Some of the tabulated results well illustrate this statement of fact. In some instances results obtained by two or more entirely different methods are recorded.

The methods of analysis adopted by the Association of Official Agricultural Chemists<sup>1</sup> were used for the analysis of food-stuffs. Total nitrogen of the urine and of the feces, the nitrogen in the phosphotungstic acid precipitate, in the xanthine silver precipitate, theobromin silver precipitate, and purine copper precipitate, was determined by the Kjeldahl-Gunning method; the nitrogen as urea was determined by the method of A. Braunstein,<sup>2</sup> and also by the well-known sodium hypobromite method, and the filtrate from the phosphotungstic acid precipitate was similarly treated; nitrogen as ammonia was determined by the method of O. Folin;<sup>3</sup> the nitrogen as uric acid by the method of E. H. Bartley;<sup>4</sup> the phosphates were determined by titration with a standardized solution of a uranium salt; sulphates were determined gravimetrically as barium sulphate, following the method of O. Folin;<sup>5</sup> the

<sup>1</sup> Bulletin No. 46, revised edition, U. S. Department of Agriculture, Division of Chemistry, "Methods of Analysis."

<sup>2</sup> A. Braunstein: *The Analyst*, 26, No. 304, p. 192.

<sup>3</sup> Otto Folin: *Ibid.*, 27, No. 310, p. 20.

<sup>4</sup> E. H. Bartley: *This Journal*, 19, 649.

<sup>5</sup> Otto Folin: *Am. Journal of Physiology*, 7, 152.

chlorine was determined by Volhard's method. In the preliminary experiments with the phosphotungstic acid solution, it was found that the separation of caffeine, from mixed solutions of urea, uric acid, hippuric acid and caffeine, was more easily and completely effected when hydrochloric acid was used in place of sulphuric acid; accordingly, the phosphotungstic acid precipitate in which the nitrogen was quantitatively determined was obtained by this method. The urine (acidified with hydrochloric acid and the precipitant were both brought to the boiling-point and thoroughly mixed; and the filtration and washing of the precipitate was carried out with a hot-water funnel. The methyl derivatives of xanthine were sought by two methods: (1) that of Martin Krüger;<sup>1</sup> (2) that of H. W. Harper: a measured quantity of urine is evaporated to dryness on a water-bath and the residue is extracted with successive portions of hot purified chloroform; this solution is treated with animal charcoal, filtered hot and the dissolved salts obtained by fractional crystallization. In one of the precipitates obtained by the method of Krüger the nitrogen was determined by the absolute method. Particular pains were taken to obtain and use nitrogen-free reagents, and the Kjeldahl-Gunning determinations were carried out, as usual, with the parallel blank. The determinations were mostly made in duplicate and triplicate. The specific gravity was taken with a pycnometer. The calculations are on the basis of O = 16 (International Table of Atomic Weights, 1902).

#### EXPERIMENTAL PART.

Mr. M. B. W., a senior student in the University of Texas, was selected for the experiment. He was twenty years of age, five feet and eleven inches high, weighing 134.5 pounds, and of exemplary habits. He had never used coffee, tea, tobacco, or alcoholic liquors, nor had he tasted chocolate in six months. Throughout the period of the experiment it was not possible for any of the methyl derivatives of xanthine to gain access to his system from without.

The experiment began at 8 A.M., Sunday, May 11th, and ended at 8 A.M., Tuesday, May 20th, continuing nine days.

The diet was planned to keep the subject in nitrogen equilib-

<sup>1</sup> Martin Krüger: *Ber. d. chem. Ges.*, 32, 2821.

rium. It contained whole milk, butter, bread, eggs, Malta-vita, sugar, lemons, and now and then a banana. An accurate account was kept of the weight of the foodstuffs consumed, and each day samples of the milk and bread were taken and the nitrogen of the same determined. The nitrogen in the Malta-vita and that in the butter was likewise determined, while that in the eggs, lemons and bananas was calculated from values given in Bulletin No. 28 (revised edition)—“The Chemical Composition of American Food Materials.”<sup>1</sup>

The experiment was divided into three periods of three days each—a period of rest, a period of excessive exercise, a second period of rest. Throughout the periods of rest the subject confined himself to the performance of his usual routine college duties. During the middle period, in addition to his usual routine, he was required each day for three days to indulge in a hurdle race until he fell exhausted.

The urine was collected in clean tared bottles, retained in a refrigerator until the output of twenty-four hours was voided, then weighed, thoroughly mixed and analyzed.

The feces corresponding to the food eaten during each of the three periods were separated in the usual manner by means of willow charcoal. Four capsules were taken with the supper of May 10th; four capsules with the breakfast of May 14th; four capsules with the supper of May 16th; and four capsules with the breakfast of May 20th. The feces between the first and second charcoal represented the first period; that including the second and third charcoal marked the second period; and that between the third and fourth charcoal marked the third period. The feces were weighed, dried at 60° C., again weighed and analyzed.

Because of a misunderstanding, the pulse and temperature were not recorded during the first two days of the experiment. The observations subsequently made are recorded below.

The letters A, B, C, D, E, F, G, H, I represent successive periods of twenty-four hours each; A, B, C represent the first period of rest, D, E, F, the middle period (period of overexertion), G, H, I, the last period (second period of rest).

The following tables include the more important results of the experiment.

<sup>1</sup> “The Chemical Composition of American Food Materials.” Bulletin No. 28, revised edition, U. S. Department of Agriculture, Office of Experiment Stations.

TABLE I.—PULSE AND TEMPERATURE DURING THE EXPERIMENT.

Before exercise.				After exercise.			
Date.	Time.	Pulse.	Temperature. °F.	Time.	Weight.	Pulse.	Temperature. °F.
C 13	7.25 A.M.	64	97.4	.....	134.5	...	...
	10.00 P.M.	60	97.2	.....	...	...	...
D 14	7.25 A.M.	62	97.4	11.00 A.M.	134.5	106	98.8
	10.15 P.M.	60	97.2	12.00 M.	...	...	90
E 15	7.25 A.M.	60	97.3	11.44 A.M.	135.0	96	98.1
	12.00 P.M.	78	98.2	12.44 P.M.	...	...	96
F 16	7.40 A.M.	50	97.6	11.35 A.M.	133.75	98	98.2
	6.30 P.M.	69	98.7	12.35 P.M.	...	...	77
	10.00 P.M.	59	97.8	.....	...	...	...
G 17	7.10 A.M.	58	97.7	.....	...	...	...
	11.25 P.M.	56	97.1	.....	...	...	...
H 18	8.15 A.M.	65	97.2	.....	...	...	...
	11.10 P.M.	52	96.3	.....	...	...	...
I 19	7.45 A.M.	62	97.2	.....	...	...	...
	2.00 P.M.	73	98.2	.....	...	...	...
	10.50 P.M.	62	97.6	.....	...	...	...

Table I is self-explanatory. The influence of the excessive exercise upon the temperature is clearly shown.

TABLE II.—WEIGHT AND NITROGEN CONTENT OF FOODS.

Food materials.	May 11, A.			May 12, B.			May 13, C.		
	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.
Milk.....	1840.3	0.432	7.9500	1864.4	0.432	8.0542	1633.9	0.565	9.2315
Eggs ....	344.4	2.112	7.2737	267.4	2.112	5.6474	270.9	2.112	5.7214
Bread ....	96.5	1.2936	1.2484	50.0	1.2936	0.6468	59.7	1.3754	0.8211
Bread ....	...	...	...	60.1	1.3754	0.8466	42.5	1.6917	0.7179
Butter ...	17.5	0.350	0.0612	15.5	0.350	0.0542	20.0	0.350	0.0700
Malta-vita	51.0	2.918	1.4881	16.0	2.918	0.4668	16.3	2.918	0.4756
Banana ..	...	...	...	...	...	...	202.0	0.208	0.4200
Sugar ....	13.8	...	...	15.0	.....	.....	6.5	.....	.....
Total N per day...	18.0214			15.7160			17.4575		

Food materials.	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.	Weight per day. Grams.	Per cent. of nitro- gen.	Weight of nitro- gen. Grams.		
May 14, D.				May 15, E.				May 16, F.			
Milk.....	1281.1	0.535	6.8552	1207.6	0.547	6.6055	1255.3	0.565	7.0924		
Eggs ....	231.8	2.112	4.8956	280.9	2.112	5.9326	309.6	2.112	6.5387		
Bread ....	148.0	1.6917	2.5037	165.0	1.688	2.7852	151.0	1.52	2.2952		
Butter ...	23.5	0.350	0.0822	54.3	0.350	0.1900	33.1	0.350	0.1158		
Malta-vita	10.3	2.918	0.3005	...	....	....	...	....	....		
Lemons..	48.0	0.160	0.0768	69.0	0.160	0.1104	68.0	0.160	0.1088		
Sugar ....	24.5	....	....	36.6	....	....	30.0	....	....		
Total N per day ...			14.7140	15.6237			16.1509				
May 17, G.				May 18, H.				May 19, I.			
Milk.....	1555.9	0.589	9.1642	789.6	0.576	4.5480	958.6	0.57	5.4640		
Eggs ....	317.9	2.112	6.7140	310.9	2.112	6.5662	304.9	2.112	6.4394		
Bread ....	54.0	1.52	0.8208	72.0	1.538	1.1073	52.0	1.213	0.6307		
Bread ....	167.0	1.538	2.5684	179.0	1.213	2.1712	179.0	1.133	2.0280		
Butter ...	41.6	0.350	0.1456	102.9	0.350	0.3601	71.9	0.350	0.2516		
Malta-vita	...	....	....	19.3	2.918	0.5631	...	....	....		
Lemons..	40.0	0.16	0.0640	46.0	0.16	0.0736	49.0	0.16	0.0784		
Bananas..	...	....	....	...	....	....	202.0	0.208	0.4201		
Sugar ....	32.0	....	....	55.0	...	....	57.0	....	....		
Total N per day ..			19.4770	15.3895			15.3122				

TABLE III.—WEIGHT AND NITROGEN CONTENT OF URINE EXCRETED.

Date, May, 1902.	Weight of urine. Grams.	Specific gravity.	Per cent. of nitrogen.			Weight of nitrogen. Grams.
			1.	2.	Average.	
11 A	1784.3	$\frac{24.0^{\circ} \text{ C.}}{24.2^{\circ} \text{ C.}}$ 1.0255	0.8623	0.8860	0.8741	15.5965
12 B	1147.3	$\frac{24.8^{\circ} \text{ C.}}{24.8^{\circ} \text{ C.}}$ 1.0316	1.3577	1.3330	1.3453	15.4346
13 C	1253.3	$\frac{24.8^{\circ} \text{ C.}}{24.8^{\circ} \text{ C.}}$ 1.0317	1.2868	1.2791	1.2829	16.0785
14 D	1193.4	$\frac{21.0^{\circ} \text{ C.}}{21.0^{\circ} \text{ C.}}$ 1.0309	1.3980	1.3857	1.3918	16.6097
15 E	1001.3	$\frac{28.8^{\circ} \text{ C.}}{28.8^{\circ} \text{ C.}}$ 1.0378	1.7301	1.6830	1.7065	17.0871
16 F	676.0	$\frac{28.2^{\circ} \text{ C.}}{28.2^{\circ} \text{ C.}}$ 1.0466	2.2260	2.2290	2.2275	15.0579
17 G	1442.3	$\frac{27.4^{\circ} \text{ C.}}{27.4^{\circ} \text{ C.}}$ 1.0285	1.1714	1.1785	1.1749	16.9455
18 H	1509.3	$\frac{24.8^{\circ} \text{ C.}}{24.8^{\circ} \text{ C.}}$ 1.0223	0.9854	0.9670	0.9762	14.5979
19 I	1294.0	$\frac{28.0^{\circ} \text{ C.}}{28.0^{\circ} \text{ C.}}$ 1.0304	1.0931	1.0650	1.0790	13.9622

A, B, C, first period of rest.....	47.1096
D, E, F, period of overexertion .....	48.7547
G, H, I, second period of rest.....	45.5056

NOTE.—Each date represents the urine collected in twenty-four hours, beginning with an empty bladder at 8.00 A.M., on the dates mentioned and including all that was passed from that time to and including that in the bladder at 8.00 A.M. the succeeding day. The analytical work began almost immediately after the last portion of each day's output was voided.

TABLE IV.—WEIGHT AND NITROGEN CONTENT OF DRIED FECES.

Weight of dried feces. Grams.	A, B, C period.		Weight of dried feces. Grams.	D, E, F period.		Weight of dried feces. Grams.	G, H, I period.	
	Per cent. of nitrogen.	Weight of nitrogen. Grams.		Per cent. of nitrogen.	Weight of nitrogen. Grams.		Per cent. of nitrogen.	Weight of nitrogen. Grams.
41.0	3.169	1.2992	6.0	2.976	0.1785	14.0	3.65	0.5110
26.0	3.434	0.8928	12.0	3.379	0.4054	11.0	3.625	0.3987
13.0	3.0526	0.3968	18.0	3.42	0.6156	32.0	3.173	1.0153
11.0	3.571	0.3928	...	...	.....	...	....	.....
Total 91.0		2.9816	36.0		1.1995	57.0		1.9250
30.3 average		0.9938	12.0 average		0.3998	19.0 average		0.6416

NOTE.—The total nitrogen of each period, divided by three, furnishes the value used in obtaining the daily nitrogen balance (see Table V).

TABLE V.—INCOME AND OUTGO OF NITROGEN.

Date, May, 1902.	Nitrogen.				
	In food. Grams.	In feces. Gram.	In food assimilated. Grams.	In urine. Grams.	Gain + or loss —. Grams.
11 A	18.0214	0.9938	17.0276	15.5965	+1.4311
12 B	15.7160	0.9938	14.7222	15.4346	—0.7124
13 C	17.4575	0.9938	16.4637	16.0785	+0.3852
14 D	14.7140	0.3998	14.3142	16.6097	—2.2955
15 E	15.6237	0.3998	15.2239	17.0871	—1.8632
16 F	16.1509	0.3998	15.7511	15.0579	+0.6932
17 G	19.4770	0.6416	18.8354	16.9455	+1.8899
18 H	15.3895	0.6416	14.7479	14.5979	+0.1500
19 I	15.3122	0.6416	14.6706	13.9622	+0.7084
A, B, C, first period of rest .....	48.2135		47.1096		+1.1039
D, E, F, period of overexertion.	45.2892		48.7547		—3.4655
G, H, I, second period of rest...	48.2539		45.5056		+2.7483

Total gain during the experiment (nine days)..... +0.3867

TABLE VI.—NITROGEN AS AMMONIA, AS URIC ACID, IN XANTHINE SILVER PRECIPITATE, IN PHOSPHOTUNGSTIC ACID PRECIPITATE, IN FILTRATE FROM THE PHOSPHOTUNGSTIC ACID PRECIPITATE TREATED WITH SODIUM HYPOBROMITE, AS UREA (a) NaOBr METHOD, (b) BRAUNSTEIN'S METHOD.

Date, May, 1902.	Ammonia nitro- gen. Grams.	Uric acid nitrogen. Gram.	Xanthine silver ni- trogen. Gram.	Phosphotungstic precipitate nitro- gen. Gram.	Phosphotungstic filtrate, NaOBr, nitrogen. Grams.	Urea (a) NaOBr, nitrogen. Grams.	Urea (b) Braun- stein, nitrogen. Grams.
11 A	*	0.3834	0.4285	0.0662	*	12.7875	**
12 B	1.4721	0.2426	0.2062	0.2158	12.7207	11.7550	12.1712
13 C	0.5108	0.2434	0.2284	0.3002	13.0275	12.2613	13.8104
14 D	0.7219	0.3385	0.4013	0.1937	13.3597	12.7995	12.9025
15 E	0.7194	0.3053	0.3252	0.5008	13.6647	10.8473	13.7192
16 F	0.4309	0.3252	0.2311	0.1548	9.0667	11.5938	11.6234
17 G	1.0817	0.3190	0.3932	0.2818	11.8519	12.9817	**
18 H	1.0186	0.2931	0.1608	0.1941	11.1050	12.4524	**
19 I	0.5988	0.2361	0.2748	0.2791	9.2599	10.9623	10.0913
A, B, C	.....	0.8694	0.8631	0.5822	(first period of rest)		
D, E, F	1.8722	0.9690	0.9576	0.8493	(period of overexertion)		
G, H, I	2.6991	0.8482	0.8288	0.7550	(second period of rest)		

NOTE.—\*Lost; \*\*results entirely too large to be trustworthy—discovered too late to make another trial by this method.

Until analytical methods exhibiting greater accuracy than now at our command are developed all attempts to produce a balance sheet of the nitrogenous constituents of the urine will prove unsatisfactory.

TABLE VII.—THE  $P_2O_5$ ,  $SO_3$ , AND  $Cl_2$  CONTENT OF THE URINE.

Date, May, 1902.	Volume, cc. at 25° C.	$P_2O_5$ , Per cent.	$P_2O_5$ , Grams.	$SO_3$ , Per cent.	$SO_3$ , Grams.	$Cl_2$ , Per cent.	$Cl_2$ , Grams.
11 A	1744.0	0.179	3.1247	0.166	2.9107	0.313	5.4714
12 B	1115.3	0.263	2.9340	0.237	2.6521	0.237	2.6489
13 C	1218.3	0.271	3.3030	0.233	2.8410	0.260	3.1742
14 D	1161.0	0.266	3.0929	0.250	2.9083	0.157	1.8314
15 E	967.5	0.324	3.1366	0.308	2.9857	0.228	2.2121
16 F	647.7	0.404	2.6218	0.410	2.6555	0.221	1.4359
17 G	1406.3	0.218	3.0657	0.197	2.7802	0.276	3.8885
18 H	1481.5	0.188	2.7948	0.174	2.5837	0.262	3.8864
19 I	1259.4	0.232	2.9250	0.197	2.4898	0.402	5.0671
A, B, C	.....	....	9.3617	....	8.4038	....	11.2945
D, E, F	.....	....	8.8513	....	8.5495	....	5.4785
G, H, I	.....	....	8.7855	....	7.8537	....	12.8420

TABLE VIII.—PERCENTAGE OF THE TOTAL NITROGEN PRESENT AS UREA, AMMONIA, URIC ACID, XANTHINE, AND PHOSPHOTUNGSTIC ACID PRECIPITATE. (Total nitrogen, 100 N<sub>2</sub>; the values given.)

	11 A.			12 B.			13 C.		
Urea (NaOBr).....	81.98	....	....	76.16	....	....	76.25	....	....
Urea (NaOBr) P.F.*.....	..	**	..	..	82.41	..	..	80.43	..
Urea (Braunstein).....	..	..	**	..	..	78.85	..	..	85.89
Ammonia.....	..	..	..	9.53	9.53	9.53	3.17	3.17	3.17
Uric acid.....	2.45	2.45	2.45	1.57	1.57	1.57	1.51	1.51	1.51
Xanthine.....	2.74	2.74	2.74	1.33	1.33	1.33	1.42	1.42	1.42
Phosphotungstic precipitate.....	0.42	0.42	0.42	1.33	1.33	1.33	1.86	1.86	1.86
Total accounted for.....	87.59	....	....	89.92	96.17	92.61	84.21	88.98	93.85
Unaccounted for.....	12.41	....	....	10.08	3.83	7.39	15.79	11.02	6.15
Total.....	100.00	....	....	100.00	100.00	100.00	100.00	100.00	100.00
			14 D.			15 E.			16 F.
Urea (NaOBr).....	77.06	....	....	63.48	....	....	76.99	....	....
Urea (NaOBr) P.F.*.....	..	80.43	..	..	79.97	..	..	60.21	..
Urea (Braunstein).....	..	..	77.68	..	..	80.28	..	..	77.25
Ammonia.....	4.34	4.34	4.34	4.15	4.15	4.15	2.86	2.86	2.86
Uric acid.....	2.03	2.03	2.03	1.78	1.78	1.78	2.15	2.15	2.15
Xanthine.....	2.41	2.41	2.41	1.90	1.90	1.90	1.53	1.53	1.53
Phosphotungstic precipitate.....	1.16	1.16	1.16	2.93	2.93	2.93	1.02	1.02	1.02
Total accounted for.....	87.00	90.37	87.62	74.24	90.73	91.04	84.55	67.77	84.81
Unaccounted for.....	13.00	9.63	12.38	25.76	9.27	8.96	15.45	32.23	15.19
Total.....	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
			17 G.			18 H.			19 I.
Urea (NaOBr).....	76.60	....	....	85.80	....	....	78.51	....	....
Urea (NaOBr) P.F.*.....	..	69.94	..	..	76.07	..	..	66.32	..
Urea (Braunstein).....	..	..	**	..	..	**	..	..	71.55
Ammonia.....	6.38	6.38	5.38	6.97	6.97	6.97	4.28	4.28	4.28
Uric acid.....	1.88	1.88	1.88	2.00	2.00	2.00	1.69	1.69	1.69
Xanthine.....	2.32	2.32	2.32	1.10	1.10	1.10	1.96	1.96	1.96
Phosphotungstic precipitate.....	1.66	1.66	1.66	1.32	1.32	1.32	1.99	1.99	1.99
Total accounted for.....	88.84	82.18	..	96.69	87.46	..	88.43	76.24	81.47
Unaccounted for.....	11.16	17.82	..	3.31	12.54	..	11.57	23.76	18.53
Total.....	100.00	100.00	..	100.00	100.00	..	100.00	100.00	100.00

NOTE.—P.F.\* means filtrate from phosphotungstic acid precipitate treated with sodium hypobromite. \*\* Lost.



TABLE IX.—RATIOS.

Date, May, 1902.	100 N <sub>2</sub> :			100 SO <sub>2</sub> : P <sub>2</sub> O <sub>5</sub> .
	P <sub>2</sub> O <sub>5</sub> .	SO <sub>2</sub> .	Cl.	
11 A	20.0346	18.6625	35.0809	107.3521
12 B	19.0092	17.1828	10.6831	110.6293
13 C	20.5429	17.6695	19.7418	116.2618
14 D	18.6210	17.5096	11.2060	106.3473
15 E	18.3565	17.4734	12.3607	105.0540
16 F	17.4114	17.6352	9.5298	98.7309
17 G	18.0915	16.4067	22.9470	110.2690
18 H	19.1452	17.6991	26.6230	108.1704
19 I	20.9494	17.8324	36.2915	117.4793
A, B, C	19.8721	17.8388	23.9751	111.3984
D, E, F	18.1547	17.5357	11.2368	103.5300
G, H, I	19.3064	17.2587	28.2207	111.8644

TABLE X.—THEOBROMINE AND PURINE BASES OBTAINED BY KRÜGER'S METHOD.

	Grams theobromine nitrogen.	Grams copper precipitate, nitrogen.
13 C	0.0325	0.0151
14 D	0.0387	0.0027
15 E	0.1245	0.0001
16 F	0.5742	0.0086
17 G	0.2932	0.0041
18 H	0.0109	0.0064
19 I	0.0782	0.0106

In order to have a permanent record of a crystalline compound present in the urine during the period of overexertion, but not found in the urine of the other periods, except in the urine of the first day succeeding the middle period, microphotographs of the crystals were made, but their publication is withheld until the compound can be definitely identified. In appearance, these crystals closely resemble crystals of caffeine and caffeine nitrate; but the yield was too small to afford a quantity of pure crystals sufficient for a combustion. A nitrogen determination (by the absolute method) was made of a mixture of the crystals obtained from urines D, E, and F, by the Krüger<sup>1</sup> method; but, on account of impurities present, the result is not conclusive beyond the demonstration of the presence of nitrogen in the compound.

In an attempt to observe the melting-point, the mass darkened but did not liquefy at 250° C., but small needle-shaped crystals

<sup>1</sup> Martin Krüger: *Loc. cit.*

were found in the upper part of the tube when examined under the microscope.

Upon incineration, the D, E, F mixture yielded 63.43 per cent. ash (mostly sodium carbonate) and 36.57 per cent. (by difference) volatile organic substance.

0.0453 gram of substance gave 2.8 cc. nitrogen at 30° C., 751 mm., = 6.35 per cent. nitrogen. On this basis, the organic matter volatilized contained 17.36 per cent. nitrogen. This is entirely too low for caffeine, but it closely approximates the amount of nitrogen found by Adolf Jolles<sup>1</sup> in the phosphotungstic acid precipitate of theophylline (17.04 per cent. nitrogen). Jolles contends that phosphotungstic acid precipitates only that portion of the purine bases in which the nitrogen is attached to the methyl groups, and that the remainder of the base is split off as urea. Thus far we have made no attempt to corroborate the work of Jolles, but shall give it attention in a subsequent investigation. On the basis of the original substance, the nitrogen found (6.35 per cent.) closely approximates the amount present in cynurenic acid— $C_{10}H_7NO_8 + H_2O = 6.76$  per cent. nitrogen; but the large amount of ash precludes this substance, as does also the method by which the crystals were obtained.

The crystals obtained by the method of Harper<sup>2</sup> from measured quantities of the corresponding twenty-four hours urine were well defined (some of them could be plainly seen with the unaided eye) but a brownish "smear" soluble in chloroform contaminated them, and the quantity obtained was too small to provide an amount of pure crystals sufficient for a combustion.

The second method is so much simpler than that of Krüger that an attempt will be made shortly to secure large quantities of this crystalline compound with a view to definitely determine its constitution.

#### SUMMARY.

1. The influence of fatigue-stuffs upon the pulse and temperature is shown in Table I. Similar observations have been repeatedly made. The subject complained of headache during the afternoon of D and the greater part of E and F.

<sup>1</sup> Adolf Jolles : *Ber. d. chem. Ges.*, 33, 2119-2121.

<sup>2</sup> H. W. Harper : In the context of this communication—Analytical methods.

2. Tables II, III, and IV are self-explanatory. The urine of the entire experiment exhibited an acid reaction, was normal in color and odor. As would be expected, the specific gravity curved upward during the middle period, and this period was also marked by a copious deposit of urates. The diazo reaction was practically uniform throughout the entire experiment. The reaction for indican was faint except in the F and G urines—these contained notable quantities; most marked in G.

3. The income and outgo of nitrogen as shown in Table V presents some very interesting features:

(a) In the food eaten the nitrogen content was largest in that of the first period, smallest in that of the middle period.

(b) The total nitrogen assimilated was largest in the third period, smallest in the middle period.

(c) The action of the digestive tract upon the nitrogenous food was greatest during the middle period, least during the first period. Of the total nitrogen in the food consumed during the successive periods 94 per cent. was appropriated during the first period, 97 per cent. during the second period, and 96 per cent. during the third.

(d) The output of nitrogen was largest during the middle period, smallest during the third period.

(e) In the nitrogen balance there was a decided loss during the middle period, a gain during the other two periods—the third period showing the largest gain. Taking the nine days' experiment as a whole the subject made a small absolute gain in nitrogen. No permanent injury resulted from the experiment.

4. The results given in Tables VI and VIII are very interesting, but their discussion had best be postponed until an absolute method for the determination of urea, when mixed with its congeners, is devised.

5. While the results given in Tables VII and IX have no direct bearing upon the production of alkyl derivatives of xanthine during excessive muscular exercise they throw some light upon the chemical aspect of metabolism, and, therefore, are of value. The output of phosphoric anhydride was greatest during the first period of rest, and least during the last period. The subject did

more mental work during the first period than during either of the subsequent periods. It should also be borne in mind that he suffered with headache during the middle period and the beginning of the third period. It is not claimed that the increase in the output of phosphoric anhydride during the first period is due to mental exertion. While such an idea naturally suggests itself, no precautions were taken to safeguard this point, and the data here presented are too meager to warrant a conclusion thereon.

The output of sulphuric anhydride was greatest during the middle period, and least during the last period. The reverse of this is shown in the case of the chlorine. The decrease in the chlorine output during the middle period is very marked, as is also its rise in the last period. As far as we know, this observation is entirely new. The amount of sodium chloride daily consumed was practically uniform throughout the three periods (nine days total). The osmotic movement from the blood to the cutaneous excretories during the period of excessive exercise may, in part, explain the facts observed; but it should be remembered that the daily period of excessive muscular exertion was of short duration.

The table showing the relative amounts of  $P_2O_5$ ,  $SO_2$ , and Cl is particularly interesting. The 100 N, :  $P_2O_5$ , Cl, and the 100  $SO_2$  :  $P_2O_5$  ratios seem to indicate that the role played by complexes containing these particular bodies is decidedly influenced by excessive exercise.

6. Evidence of the presence of methyl derivatives of xanthine is presented in Table X. This evidence finds further support in the microphotographs of a crystalline substance obtained from the phosphotungstic acid precipitate by the method of Krüger, and of those obtained by the chloroform method. The quantity of crystals obtained in a state of purity was insufficient for a combustion. However, a nitrogen determination (by the absolute method) was made of some of the contaminated crystals that we might at least prove or disprove the presence of nitrogen in the compound. The results obtained are given. It will be seen that the nitrogen is too low for any of the known methyl derivatives of xanthine. In the context will be found a fuller discussion of this point.

7. Thus far this investigation has thrown some new light upon the chemistry of fatigue, but much additional work is yet to be done before the theoretical discussion of the results may be profitably entered upon. The inquiry will be further pursued in this laboratory.

In conclusion the authors acknowledge their sincere thanks for assistance rendered by Messrs. F. C. Beall, O. D. Hargis, H. Kuehne, and M. B. Wesson.

**NOTE.**—This communication is dated June, 1902, because the experimental part was complete by that time. However, the results were not put in their present shape for publication until September, 1902, the duties incident to the close of the session making it impossible to shape the results at an earlier date.

THE UNIVERSITY OF TEXAS, CHEMICAL LABORATORY,  
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## ON THE FIXATION OF AMMONIA AND POTASH BY HAWAIIAN SOILS.

BY J. T. CRAWLEY AND R. A. DUNCAN.

Received September 30, 1902.

IN this Journal, 24, 1114, will be found a paper by the writer on the "Fixation of Phosphoric Acid in the Soil." This paper will record results on the fixation of the other chief fertilizer constituents, ammonia and potash. The same methods described in that work were followed in these experiments, and the results, therefore, can be compared with each other. The main object is to find the depth in the soil at which the chief fertilizing materials are fixed and to determine the loss by drainage when the application is followed by a heavy irrigation. A given weight of the commercial article containing ammonia and potash, namely, sulphate of ammonia and sulphate of potash, is applied to the soil, and this is irrigated with 3 or 4 inches of water (the usual irrigation as practiced on the plantations), the drainage collected and analyzed. The difference between the amount applied and that found in the drainage is the amount abstracted or held by the soil. By varying the depth of soil we find the depth at which the ingredients are fixed. Boxes (9 inch cube) with holes in the bottom for the escape of water were used in the experiment. In all cases

4800 cc. of water were poured upon the soil, and the time necessary for the excess to drain off is given.

#### I. FIXATION OF AMMONIA.

Ten grams of commercial sulphate of ammonia, containing 2.478 grams ammonia were used in each case.

(1) Six inches of soil; the sulphate was scattered over the soil and 4800 cc. water were added; 1130 cc. drained through within seventeen minutes, containing 0.0038 gram ammonia or 0.155 per cent. of total applied.

(2) Four inches of soil; drainage was completed in twelve minutes; 2180 cc. water passed through, containing 0.0464 gram ammonia or 1.387 per cent. of total.

(3) Two inches of soil; drainage was completed in thirteen minutes; 3280 cc. water were recovered, containing 0.3400 gram ammonia, or 13.88 per cent of total.

(4) One inch of soil; drainage was completed in seventeen minutes; 4000 cc. water were recovered, containing 1.2328 grams ammonia, or 49.79 per cent. of total.

Putting these results together, we have:

TABLE I.—FIXATION OF AMMONIA.

Depth of soil. Inches.	Ammonia retained. Per cent.
6	99.85
4	98.13
2	86.12
1	50.21

In these experiments we see that with irrigation following the application of sulphate of ammonia, one-half is retained in the first inch, more than four-fifths within the first 2 inches and almost all within 4 inches of soil.

In order to determine if the ammonia retained has been firmly fixed and is insoluble in water, the 1 inch of soil which had already been irrigated once was subjected to further irrigations, with the following results:

TABLE II.—AMOUNT OF AMMONIA WASHED FROM THE FIRST INCH OF SOIL BY SUCCESSIVE IRRIGATIONS.

Number of irrigations.	Ammonia washed out. Grams.	Per cent.
First.....	1.2328	49.79
Second, three days after first.....	0.1937	7.8
Third, one hour after second.....	0.1249	5.0
Fourth, nineteen hours after third...	0.0904	3.6
Fifth, one hour after fourth .....	0.0581	2.3
Total, five irrigations.....	1.6999	68.49

The ammonia is held rather firmly, but subsequent irrigations wash it out in decreasing quantities.

## II. FIXATION OF POTASH.

Ten grams sulphate of potash containing 4.8 grams actual potash were scattered over the soil, and water was poured over, as in preceding tests.

TABLE III.—FIXATION OF POTASH.

Depth of soil. Inches.	Potash retained. Per cent.
6	98.55
4	94.18
2	82.03
1	69.19

Seven-tenths of the potash applied is retained in the first inch, more than four-fifths in 2 inches and almost all within 6 inches of the soil. The box containing 6 inches of soil which had been irrigated once, was subjected to further irrigations to see if the potash is held firmly.

TABLE IV.—AMOUNT OF POTASH WASHED FROM SIX INCHES OF SOIL BY SUCCESSIVE IRRIGATIONS.

Number of irrigation.	Potash washed out. drainage.		
	Grams.	Per cent.	Grams.
First .....	0.0697	1.45	0.0680
Second, 4 days after first .....	0.1631	3.4	0.2044
Third, 1 hour after second .....	0.1659	3.5	0.0361
Fourth, 16 hours after third .....	0.1302	2.7	0.0296
Fifth, 1 hour after fourth .....	0.1139	2.4	0.0243
Sixth, 7 days after fifth .....	0.0929	1.9	0.0251
Seventh, 2 days after sixth .....	0.0948	2.0	0.0228
Eighth, 7 days after seventh .....	0.0967	2.0	0.0215
Total, 8 irrigations .....	0.9272	19.35	

As the moisture content of the soil varies, the amount of drainage will vary. Therefore I have included in the table the amount of potash in each 1000 cc. of drainage. As in the case of ammonia, the potash is held rather firmly but irrigations gradually wash it away, light irrigations having washed 19 per cent. out of 6 inches of soil.

Below will be found the results on phosphoric acid, ammonia, and potash.

TABLE V.—FIXATION OF PHOSPHORIC ACID, AMMONIA AND POTASH.

Depth of soils.	Phosphoric acid retained. Per cent.	Ammonia retained. Per cent.	Potash retained. Per cent.
6	99.43	99.84	98.55
4	....	98.13	94.18
3	91.25	....	....
2	....	86.12	82.03
1	53.35	50.21	69.19

These results have a great practical bearing on plantation work in these islands. Many of the plantations depend upon irrigation entirely, and a great deal of the water, as I have shown in an article in the August number of the *Hawaiian Planter's Monthly* on "The Water-Holding Power, and the Irrigation of Hawaiian Soils," passes directly and immediately through the soils. In other cases, as in the Hilo district, the soils are subjected to very heavy rains. Were the soluble fertilizer ingredients not fixed at once the loss would be very great; but the experiments show that even under heavy washings they are fixed very rapidly. But the solubility of these substances in water after the first irrigation, though slight, emphasizes the importance of keeping the irrigation well under control. The nitrogen of sulphate of ammonia is gradually changed to nitrate, and most of that which the plant has not assimilated is washed away by the first irrigation or heavy rainfall. The phosphoric acid is more firmly bound, and the loss of this substance is very slight. Under the conditions of the tests, 19 per cent. of the potash applied as sulphate was washed below 6 inches by eight irrigations.

We thus see that heavy and repeated irrigations wash out the available ammonia and potash; and this will partially account for the fact that very often the effects of a fertilizer, especially of a nitrogenous fertilizer, are not lasting.

HONOLULU, H. I.

## A PROBABLE CAUSE OF THE DIFFERENT COLORS OF IODINE SOLUTIONS.

BY ARTHUR LACHMAN,

Received September 30, 1902.

It is a well-known fact that solutions of free iodine have different colors, depending in some way upon the nature of the solvent.



Gautier and Charpy,<sup>1</sup> who investigated this problem about twelve years ago, distinguished four sets of colors, of the following types:

- (1) Violet, *e. g.*, chloroform; (2) red, *e. g.*, ethylene bromide; (3) red-brown, *e. g.*, toluene; (4) brown, *e. g.*, alcohol.

A large number of solvents were thus classified, but the authors confessed themselves unable to find any relations between the chemical function of the solvent and the color. The following year, Rigollot<sup>2</sup> determined the absorbing power of different iodine solutions for definite light-waves; but his results led to no explanation. A few years later, an elaborate study of the problem was undertaken by Krüss and Thiele<sup>3</sup>. They ascertained the molecular weight of iodine in various solvents, and found that practically in all cases, where moderately dilute solutions were taken, the iodine molecule consists of 2 atoms. Variations from this value were irregular, both for brown and for violet solutions. Concentrated solutions usually gave high molecular weights, indicating association, but no change of color accompanied this association.

In spite of these results, Krüss and Thiele attempt to explain the different colors by an assumption of different molecular weights: violet solutions containing  $I_2$ , brown solutions  $(I_2)_n$ ,  $n$  being greater than 1. These complicated molecules, however, are supposed to give a normal molecular weight by all osmotic methods. This explanation is equivalent to saying that in brown solutions the molecular weight of iodine is much greater than in violet, but that none of our present methods are able to demonstrate the increase; and it involves a conception of the molecular theory whose utility yet remains to be shown. The change from brown into violet is ascribed to dissociation; if the above theory is correct, solvents with brown color should have less dissociating power than those with violet. But this is contradicted by well-established facts; alcohol has much greater dissociating power than chloroform or benzene.

Notwithstanding the negative results of Gautier and Charpy, and of Krüss and Thiele, a simple causal connection seems to exist between the chemical behavior of the solvent and the color

<sup>1</sup> *Compt. Rend.*, 110, 189; 111, 645 (1890).

<sup>2</sup> *Ibid.*, 112, 38 (1891).

<sup>3</sup> *Ztschr. anorg. Chem.*, 7, 25 (1894).

of iodine solutions. This relationship was not apparent to the above investigators *because in critical cases they observed wrong colors*, owing to impurities in the solvents. From the table given below, it will be seen that iodine solutions, when made with pure solvents have but two colors—violet and brown—with but one exception, which will be discussed below.

#### COLOR OF IODINE IN VARIOUS SOLUTIONS.

##### A. Violet Solutions.

###### Hydrocarbons :

Hexane  
Benzene (thiophene free)  
Toluene<sup>1</sup>  
*o*-Xylene<sup>2</sup>  
*m*-Xylene  
*p*-Xylene

###### Halogen compounds :

Chloroform  
Ethylene chloride<sup>3</sup>  
Ethylidene chloride  
Tetrachlorethylene<sup>4</sup>  
Carbon tetrachloride  
Isobutyl chloride<sup>5</sup>  
Amyl chloride  
Chlorobenzene  
Benzalchloride  
Benzotrichloride

Bromoform  
Ethylene bromide<sup>6</sup>  
Trimethylene bromide  
Amyl bromide<sup>6</sup>  
Brombenzene

###### Nitro compounds :

Nitroethane  
Nitropropane  
Tetranitromethane  
Isobutyl nitrate

###### Sulphur compound :

Carbon bisulphide

<sup>1</sup> Gautier-Charpy, red-brown.

<sup>2</sup> Thiele-Krüss, wine-red (xylenes not separated).

<sup>3</sup> Gautier-Charpy, Krüss-Thiele, red.

<sup>4</sup> Tetra-chlorethylene,  $C_2Cl_4$ , is the only substance in the above list which is unsaturated in structure. Its easy formation during chlorination reactions indicates that its unsaturated character is more formal than real, in spite of its double bond.

<sup>5</sup> Ethylene bromide, amyl bromide, and isobutyl chloride required careful purification before giving violet solutions. The impure solvents, which gave red solutions, all decolorized permanganate.

<sup>6</sup> Gautier-Charpy, Krüss-Thiele, red.

##### B. Brown Solutions.

###### Iodides :

Ethyl iodide  
Amyl iodide  
Cetyl iodide  
Phenyl iodide  
Potassium iodide { In water  
Hydrogen iodide { solutions  
Oxygen compounds.

###### Alcohols :

Methyl alcohol  
Ethyl alcohol  
*n*-Butyl alcohol  
Dimethylethyl carbinol  
Heptyl alcohol

###### Ethers :

Ethyl ether  
Dimethyl acetal  
Anisol  
Phenetol

###### Ketones :

Acetone  
Methylethyl ketone  
Diethyl ketone  
Acetaldoxime  
Acetophenone

###### Acids and esters :

Formic acid  
Acetic acid  
Lactic acid  
Caproic acid  
Ethyl acetate  
Amyl acetate  
Isobutyl isobutyrate

###### Sulphur compounds :

Amyl mercaptan  
Thiophene  
Nitrogen compounds.

###### Nitriles :

Acetonitrile  
Propionitrile  
Capronitrile  
Benzonitrile

###### Nitrilo-bases :

Pyridine  
Quinoline

From the results tabulated above, all of which have been verified personally, the relationship between color and the constitution of the solvent stands out clearly: *saturated solvents give violet, solvents which have unsaturated character give brown solutions.* In the first, or violet class, we find hydrocarbons, their chlorides and bromides, and carbon bisulphide; and also, strange to say, the *nitro compounds*. All the other oxygen compounds, so far as investigated, give brown solutions. The brown solvents comprise the alcohols, ethers, ketones, acids and esters; nitriles and nitrilo-bases; alkyl and other iodides; and bivalent sulphur compounds.

The iodine molecule, as found in iodine vapor, is violet; we have every reason for assuming that in its violet solutions iodine is in a state of normal physical distribution. On the other hand, certain of the brown solutions are known to contain periodides, usually of the form  $(MX).I_2$ ; among these are potassium iodide, phenyl iodide, and the tertiary bases. Nitriles have long been known for their additive properties in general; and in the case of oxygen compounds, the recent startling results of Baeyer and Villiger<sup>1</sup> have fully demonstrated the hitherto unsuspected additive powers of combined oxygen atoms. It seems quite justifiable to assume in all brown iodine solutions the existence of (probably unstable) addition products whose general composition is



Such an explanation was indeed offered some years ago by Beckmann,<sup>2</sup> and considered and rejected by Krüss and Thiele. If it is assumed, as it was by Beckmann, that the *whole* of the iodine thus adds to the solvent, the effect upon the *observed* molecular weight would be a marked decrease (as a consideration of Raoult's formula shows), contrary to the measurements of Krüss and Thiele. But there is no need to make this assumption; a very small amount of alcohol suffices to change the color of an iodine-chloroform solution, and 3 per cent. of alcohol give as dark a brown as can be obtained with pure alcohol.

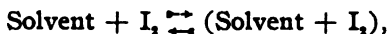
#### EFFECT OF ABSOLUTE ALCOHOL ON COLOR OF IODINE IN CHLOROFORM.

Alcohol.	Per cent.	Color.
	3.5	Brown
	0.4	Red
	0.2	Mixed red and violet
	0.1	Violet

<sup>1</sup> *Ber. d. chem. Ges.*, 34, 2679 (1901).

<sup>2</sup> *Ztschr. phys. Chem.*, 8, 76 (1889).

The iodine in brown solutions is therefore probably in a condition of equilibrium between pure solution and the addition product



very much like many double salts, or like the chlorine ions<sup>1</sup> in green chromium chloride hexahydrate.

The view here presented, that brown solutions contain some addition product, and violet solutions simple iodine molecules, is borne out by an important fact: Brown solutions tend to become violet when heated, and conversely, violet solutions become brown on being cooled sufficiently.<sup>2</sup> As heat produces dissociation, and cold induces association, the facts are in excellent agreement with expectation.

The actual isolation of the addition products of iodine with oxygen compounds will probably be difficult, but an effort in this direction will be made as soon as possible. Schützenberger<sup>3</sup> has described an addition product of bromine and ether, and iodine may behave similarly.

Two points remain for discussion. In the first place, the behavior of the nitro compounds seems to put them apart from other oxygen compounds. The structure of the nitro group is still uncertain, but numerous reactions show that its oxygen atoms are quite active, and possess considerable additive power.<sup>4</sup> Their indifference to iodine will be investigated more closely later on.

The second point is the behavior of ethyl bromide towards iodine. In spite of numerous efforts, I have not been able to prepare this substance in a state sufficiently pure to obtain with it a violet iodine solution; in every case, the solution is dark red. Ethyl bromide is made by two methods; the distillation of ethyl-sulphuric acid with potassium bromide also forms ether, which cannot be separated by the most careful fractioning; and the action of phosphorus bromide upon alcohol yields ethyl bromide contaminated with phosphorus, which resists hours of boiling with moist sodium amalgam. I am confident, however, that ethyl bromide will prove no exception to the above classification of

<sup>1</sup> Werner: *Ber. d. chem. Ges.*, 34, 1579 (1901).

<sup>2</sup> Krüss and Thiele: *Loc. cit.*, p. 78; Gautier and Charpy: *Compt. Rend.*, 111, 645 (1890); Wiedemann: *Wied. Ann. Phys.*, 269, 590.

<sup>3</sup> *Compt. Rend.*, 78, 1511 (1873); *Ann. Chem.* (Liebig), 167, 86 (1873).

<sup>4</sup> Lachman: *Am. Chem. J.*, 21, 443 (1899); This Journal, 23, 897 (1901); Angeli: *Ber. d. chem. Ges.*, 29, 1884 (1896); Meisenheimer: *Ann. Chem.* (Liebig), 323, 205 (1902).

iodine solvents, for similar difficulties were met, during this investigation, with amyl bromide and ethylene bromide. The first samples of these substances gave dark red iodine solutions, but after careful purification, pure violet solutions were obtained.

SAN FRANCISCO, September 13, 1902.

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[CONTRIBUTIONS FROM THE NEBRASKA EXPERIMENT STATION, NO. I.—  
SENT BY E. A. BURNETT.]

### PRUSSIC ACID IN SORGHUM.

BY HENRY B. SLADE.

Received October 3, 1902.

INSTANCES of the fatal effects of green sorghum upon stock are frequently reported. The Nebraska Experiment Station records 144 fatal cases in a single year. "At Imperial 10 cattle out of a herd of 32 died suddenly. At Culbertson 11 cattle died within an hour from eating cane. At Wauneta a stockman reports the loss of 7 head out of a small herd."<sup>1</sup> From Australia like cases are reported.<sup>2</sup> In one instance 17 animals in a single herd died from eating sorghum; in other instances cattle were allowed to feed upon the cane without loss. Berthelot and André in 1886, in an article on "The Noxious Effects of Sorghum,"<sup>3</sup> ascribed the cause to excessive amounts of potassium nitrate. The late Mr. Williams, of the U. S. Department of Agriculture, also suggested saltpeter as the cause of the trouble.<sup>4</sup> Determinations of the potassium nitrate in poisonous sorghum by Hiltner<sup>5</sup> showed that the amount present was inadequate to the effect produced and the idea was presented that "the plant under certain conditions develops a highly poisonous chemical compound." In a paper before the Nebraska Section of the American Chemical Society<sup>6</sup> the theory was put forward by the writer, in the fall of 1901, that such a poisonous compound might be produced by the action of an enzyme upon a glucoside formed in the plant through a process of abnormal growth.<sup>7</sup> An examination of a sample of sorghum

<sup>1</sup> Nebraska Experiment Station Bulletin No. 63.

<sup>2</sup> Quoted in Experiment Station Record, 13, 992.

<sup>3</sup> Abstract in Biedermann's *Centralblatt*, 22, 470.

<sup>4</sup> Farmers' Bulletin No. 50, p. 17.

<sup>5</sup> Nebraska Experiment Station Bulletin No. 63.

<sup>6</sup> Nebraska Experiment Station, 15th Annual Report, p. 55.

<sup>7</sup> Dunstan and Henry have since confirmed this view in the case of the Great Millet or Sorghum Vulgare of Egypt. Since the above article was contributed the attention of the

from a lot which had proved fatal to cattle showed the presence of prussic acid. A further study appears to verify the view that the acid is split off from a compound through ferment action and a preliminary report of the results is now given.

The sample in question was received at the Station the fourth day after it had been cut. A portion was crushed by means of a sausage grinder, macerated with water for an hour and the filtered extract distilled into sodium hydroxide. On the addition of ferrous and ferric salts and acidulating with hydrochloric acid the characteristic blue color of the ferrocyanide of iron was obtained. The test was repeated with separate stalks with like results in every case. The prussic acid was also obtained as the nitroprusside and as silver cyanide. No prussic acid could be obtained from the water extracts of the roots but leaves and stalks both gave good tests, more marked in the stalks which appeared to yield the greater amount of the acid.

The same sample after drying in the laboratory for twelve days still yielded a decided test for prussic acid. Another sample of sorghum cut at the same time and cured in the field for six days and in the laboratory for twelve days likewise produced the acid on following the same procedure as in the other cases. The fact that the sorghum, if dried without crushing, still retains the power to produce prussic acid indicates the localization of the enzyme and acid-producing compound in separate cells of the plant. Quantitative estimations of the yield of prussic acid were made by macerating single stalks in a crushed condition for twelve hours in rubber-stoppered flasks. The acid formed was distilled into dilute sodium hydroxide and the amount of cyanide determined by titration with silver nitrate according to Liebig's method as directed by Fresenius.<sup>1</sup> By this procedure 0.013 per cent. of prussic acid was obtained in one case and 0.014 per cent. in

the other. The writer has been called to the work of the two English investigators who have isolated a glucoside, dhurrin, which breaks up under the action of an enzyme with the formation of prussic acid. (*Chemical News*, June 27, 1902.) From the brief account of the properties given, dhurrin does not seem to be identical with the prussic acid-forming glucoside of American cane. Dr. Samuel Avery, of the Nebraska Agricultural Experiment Station, in a private communication to the writer, states that under certain conditions the glucoside from American sorghum is decomposed by boiling hot water, which is not the case with dhurrin. It would be interesting to know whether the various glucosides yielding prussic acid form a chemical series similar to those of the saponin bodies worked out by Robert.

<sup>1</sup> "Quantitative Analysis," p. 450.

another. On this basis a kilogram of sorghum would contain over twice the maximum medicinal dose for cattle, of the anhydrous acid and might prove fatal. Frohner<sup>1</sup> places the fatal dose at 0.5 to 1 gram. At this rate 3.5 kilos of the cane would be extremely dangerous. A cow turned into the patch from which the above samples were taken developed the most marked symptoms of prussic acid poisoning after eating only a small amount of the cane. In the light of these results there would seem to be but little question that the poisoning of stock by sorghum is due to the prussic acid yielded by the plant.

The question still remains as to the formation of the prussic acid in the sorghum. Robiquet and Boutron-Charlard<sup>2</sup> found prussic acid in oil of bitter almonds, and in 1837 Liebig and Wöhler<sup>3</sup> discovered that the prussic acid was formed by the action of the emulsin upon the amygdalin in the almonds. Since that time prussic acid has been found in various plants and its formation has been generally ascribed to the action of emulsin upon some glucoside. In 1900 Dunstan and Henry<sup>4</sup> discovered a new prussic acid-producing enzyme in the Egyptian vetch (*Lotus arabicus*) which they call lotase. Lotase splits up the glucoside, lotusin, with the production of prussic acid, a yellow coloring-matter, lotoflavin, and dextrose. Cattle in Northern Africa are oftentimes fatally poisoned by eating the vetch up to the time of the ripening of the seed. After that time the glucoside disappears and the plant becomes harmless.<sup>5</sup>

In the case of sorghum the poison seems to be formed by the action of an enzyme upon a glucoside. The fact that the dried plant still yielded prussic acid shows that it does not exist in that form in the plant. To determine whether the acid was formed by chemical or ferment action, extracts were made by digesting 20 grams of the sorghum pulp with 250 cc. of water at the temperature of the laboratory and also by pouring boiling hot water upon a like amount of pulp and boiling for five minutes. Both were allowed to macerate and then distilled as usual into

<sup>1</sup> "Lehrbuch der Toxicologie," p. 860.

<sup>2</sup> Quoted by Oppenheimer: "Ferments and Their Actions," English translation, p. 209.

<sup>3</sup> *Ann. Chem. Pharm.*, 21, 96; 22, 17.

<sup>4</sup> *Royal Society Proceedings*, 67, 224; 68, 374.

<sup>5</sup> Thanks are due to Mr. V. K. Chesnut, of the poisonous Plants Division of the U. S. Department of Agriculture, for this reference.

sodium hydroxide. The former gave the usual marked test for the acid but the extract which had been boiled gave only the slightest trace of acid, the acidulated solution yielding only a faint green color after standing for some time. The formation of the prussic acid hence appeared due to a ferment action. However, as the compound producing the acid might be decomposed by simply boiling and the prussic acid formed thereby escape, extracts were also prepared with 95 per cent. alcohol, 2 per cent. sodium hydroxide, 0.4 per cent. hydrochloric acid, 0.2 per cent. sodium carbonate and 0.5 per cent. sodium chloride. In each of these tests 20 grams of the sorghum pulp and 250 cc. of the solvent were taken and a few drops of chloroform added to prevent bacterial action. The sorghum was introduced into the solvent so soon as it had been reduced to a pulp with a sausage grinder and the digestion continued for three days in glass-stoppered bottles at the room temperature; the liquid rapidly filtered through linen into a flask and distilled into sodium hydroxide. In the case of the alkaline extracts the liquid was rendered acid with dilute sulphuric acid before distilling. Neither the acid nor alkaline extracts showed a trace of prussic acid as was also the case with the alcoholic extract. On the other hand the sodium chloride extract gave a distinct test. If the formation of the acid were due to simple chemical decomposition through boiling, tests for the acid should have been obtained in every case. On the other hand the slight trace only of acid found in the boiled extract and the known hindering action of acids and alkalies as well as the favorable action of sodium chloride upon ferment action point to this as the source of the prussic acid. The behavior of the ferment in these respects would serve to identify it as emulsin but an extract with 40 per cent. alcohol yielded prussic acid while emulsin is sensitive to the presence of 8 per cent. alcohol.<sup>1</sup> In studying the enzymes of sorghum the active preparations from the plant had no action upon amygdalin, from which the absence of emulsin was inferred.<sup>2</sup> The active agent in this case may be a special form of emulsin such as that described by Jorissen and Hairs<sup>3</sup> or possibly a new enzyme. It does not appear to be ordinary emulsin. The glucase of sorghum acts upon

<sup>1</sup> Effront: "Enzymes and Their Applications," English translation, 1, 270.

<sup>2</sup> Nebraska Experiment Station, 15th Annual Report, p. 61.

<sup>3</sup> Quoted by Oppenheimer, p. 210.



glucosides and with amygdalin produces no prussic acid. The action of glucase, however, is not hindered, apparently, by hydrochloric acid.

From the above sample of poisonous sorghum, an enzyme preparation was obtained by precipitating the sorghum juice with 95 per cent. alcohol and again precipitating the alcoholic filtrate. The impure preparation thus obtained gave a decided blue color, which rapidly developed, with freshly-prepared tincture of guaiac and hydrogen peroxide but not after boiling the solution of the ferment. With various preparations from the sorghum this formed no prussic acid. The same preparations likewise gave negative tests for the acid after boiling with dilute mineral acids, neutralizing and testing with Fehling's solution. In every case where prussic acid was formed, the extract gave a rose-red color with strong hydrochloric acid in excess or with concentrated sulphuric acid. In the extracts where no prussic acid was formed no such reaction could be obtained. The most intense color was obtained from the water extracts of the stalks which was prepared by cutting off the stalks for four inches above the roots into small, quarter-inch pieces and macerating with water for an hour. This substance appears to be a coloring-matter formed together with the prussic acid by enzyme action. With alkalies the color produced by the acid disappears and returns on acidulating. With nitric acid the red color disappeared and on reducing the red hydrochloric acid solution of the substance with zinc dust no color appears on neutralizing.

This coloring-matter is precipitated by lead subacetate from which it may be again obtained by treating the precipitate suspended in water with hydrogen sulphide and treating the lead sulphide with hydrochloric acid. By filtering, neutralizing and extracting the residue with alcohol the compound may be isolated. The lead precipitate gives the characteristic brilliant rose-red with hydrochloric and sulphuric acids.

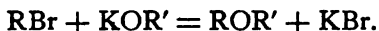
Thus far the suspected glucoside of American cane has not been isolated and the evidence for its existence rests upon the formation of prussic acid and a coloring-matter under the conditions described together with the general experience of the formation of prussic acid in plants. The evidence thus far at hand points to ferment action as the cause.

## DERIVATIVES OF PHENYLETHER. V.

BY ALFRED N. COOK.

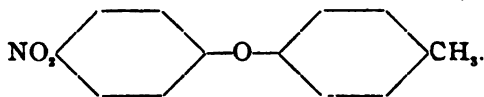
Received October 6, 1908.

For some time past I have been engaged in the study of the derivatives of phenylether, using a reaction that is of common application in both the fatty and aromatic series, that of treating a fatty or aromatic haloid with an alcoholate or phenolate of an alkali metal. An ether is formed and an alkali salt of a haloid acid is precipitated according to the following equation:



It has been found<sup>1</sup> that an aromatic bromide or chloride containing a nitro group in the ortho or para position reacts with great readiness upon potassium phenolates to produce derivatives of phenylether. During the past three years I have extended this method to the cresols. Success has attended each attempt to combine a potassium cresolate with a bromnitrobenzene, and each of the mother substances has yielded a number of derivatives.

### 4-NITRO-4'-METHYL PHENYLETHER,



This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared as described in a previous article.<sup>2</sup>) Equimolecular quantities of the two reacting substances were heated together in an oil-bath. Action began at 110°, as was shown by the agitation of the fused mass, and rose during the action to 125°. The phenylether could not be extracted from the precipitated potassium bromide with ethyl ether as had been previously done with its analogues, on account of its sparing solubility in that menstruum, and it was found that the substance could be separated from the parabromnitrobenzene not acted upon, and other substances, by simple fractional distillation under diminished pressure, instead of distilling them off with steam as had been previously done in analogous cases. The

<sup>1</sup> *Ber. d. chem. Ges.*, 29, 1446 and 1878.

<sup>2</sup> *Am. Chem. J.*, 24, 526.

method was afterwards found to give good results with other analogues, as has already been described in the two previous papers. The yield was about 1.25 grams of the nitromethylphenylether for every gram of the cresol used. After purifying as much as possible by repeated fractional distillation *in vacuo*, it was crystallized several times from hot alcohol.

4-Nitro-4'-methyl phenylether is a sulphur-yellow, crystalline substance which speedily turns brown on exposure to light, and melts at 66°. It is soluble in benzene, sparingly soluble in sulphuric ether, and insoluble in petroleum ether. It is much less soluble in cold than in hot alcohol which renders it very readily crystallized. It boils at 225° under a pressure of 25 mm. It has no taste but feels like sulphur when taken into the mouth. It had an odor of parabromnitrobenzene from which it could not be freed by fractional distillation and repeated crystallization from alcohol. An attempt to oxidize the side-chain to carboxyl by means of chromic acid in acetic acid solution was unsuccessful. The substance was entirely destroyed. An analysis gave 6.27 per cent. N; calculated, 6.11 per cent.

4-NITRO-4'-METHYL PHENYLETHER SULPHONIC ACID,



was prepared by the same method as its analogues described in previous papers. When a solution of the acid was evaporated to a small bulk it separated as a thick, red, syrupy liquid which, when dissolved in hot water, crystallized in light yellow needles which melted at 102°. A water solution is much yellower than the substance itself. 8.4 parts of the acid are soluble in 1000 parts of water at 80°. The purified acid is almost tasteless in the solid form, while the syrupy liquid has a sharp odor and taste, probably due to decomposition products formed during evaporation. Its composition was determined by the analysis of the barium salt.

The barium salt,  $(\text{CH}_3.\text{NO}_2.\text{C}_{12}\text{H}_7\text{O}.\text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$ , was prepared by the method described in previous papers. It crystallizes from a water solution in warts of a light yellow color which turn brown on exposure to light, if but slightly moist. The substance has a bitter taste and its water solution is yellow. 20.8 parts of the salt are soluble in 1000 parts of water at 15°, and

128.6 parts are soluble in 1000 parts of water at the temperature of the boiling water-bath. When heated in the air-bath at  $100^{\circ}$  it turns to a sulphur-yellow color and loses in weight corresponding to 1 molecule of water of crystallization. At this stage it is hygroscopic and when exposed to the air increases to its original weight. When heated to  $168^{\circ}$  it loses in weight corresponding to a second molecule of water and becomes white. At this stage it is not hygroscopic. The loss in weight is permanent. Two analyses of the salt desiccated over sulphuric acid resulted as follows:

	Calculated for ( $C_{12}H_{10}O_6NS$ ) <sub>2</sub> Ba + 2H <sub>2</sub> O.	I.	Found. II.
Barium.....	17.36	17.29	17.21
Water at $100^{\circ}$ .....	2.28	2.46	2.49
Water at $168^{\circ}$ .....	2.28	2.23	2.33

The sodium salt,  $CH_3.NO_2.C_{12}H_7O.SO_3Na + 3\frac{1}{2}H_2O$ , was prepared by precipitating the barium from a water solution of the barium salt with sodium carbonate. The water solution is more intensely yellow than that of the barium salt. On evaporating to a small bulk it crystallized out in radial aggregations of leaf-like crystals. It is soluble in alcohol and 62 parts of the salt are soluble in 1000 parts of water at  $20^{\circ}C$ . After desiccation over sulphuric acid it was heated in the air-bath to  $100^{\circ}$ , when it lost in weight corresponding to 3.5 molecules of water of crystallization. Two determinations of the water of crystallization resulted as follows:

	Calculated for $C_{12}H_{10}O_6NSNa + 3\frac{1}{2}H_2O$ .	I.	Found. II.
Water.....	15.99	15.97	15.97

4-AMINO-4'-METHYL PHENYLETHER,  $NH_2.C_6H_4.OC_6H_4.CH_3$ , was prepared from the hydrochloride salt mentioned below by precipitating from a water solution with ammonium hydroxide. It is a snow-white substance which is soluble in alcohol, insoluble in ether, and melts at  $122^{\circ}$ . It is soluble in hot water from which it crystallizes on cooling in white flakes.

The hydrochloride salt was prepared from the corresponding ether by reducing with tin and hydrochloric acid in alcoholic solution while warming on the water-bath, and precipitating the tin with hydrogen sulphide. It showed some tendency to decompose while evaporating to crystallization. It is very soluble in water

but does not crystallize from it successfully. It crystallizes readily from a hot solution of strong hydrochloric acid in long needles or glistening flakes.

The *hydrobromide* was formed by dissolving the free amino compound in hydrobromic acid. Its appearance is very much like the hydrochloride. The amino compound dissolves with some difficulty in dilute sulphuric acid to form the *sulphate*. It crystallizes out in glistening flakes. The *nitrate*, formed in a similar manner, crystallizes from the acid solution, on cooling, in flat needles.

The *platinum salt*,  $(\text{CH}_3\text{C}_6\text{H}_4\text{OC}_6\text{H}_4\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$ , was prepared by adding a solution of chlorplatinic acid to a strong solution of the hydrochloride. It does not precipitate immediately, unless the solutions are very strong, but in a few minutes fine yellow crystalline needles are formed. When moist it turns brown in diffused light, but when dry the direct sunlight does not affect it. The melting-point is  $195^\circ$ . When heated to  $100^\circ$  in an air-bath it became dark colored and lost in weight corresponding to 1 molecule of water of crystallization. Analyses for platinum and water resulted as follows:

	Calculated for $(\text{C}_{13}\text{H}_{13}\text{NO})_2\cdot\text{H}_2\text{PtCl}_6 + \text{H}_2\text{O}$ .	I.	Found. II.
Platinum.....	23.61	23.40	23.85
Water at $100^\circ$ .....	2.18	2.47	....

NITRO-4-NITRO-4'-METHYL PHENYLETHER,  $(\text{NO}_2)_2\text{CH}_3\text{C}_6\text{H}_4\text{O}$ .

Strong nitric acid was added to a quantity of 4-nitro-4'-methyl phenylether when the temperature rose  $2^\circ$ - $3^\circ$  and the acid turned to a reddish color, the ether apparently dissolving slightly in the acid. On heating to  $80^\circ$ - $90^\circ$  a violent action began, dense brown fumes being given off, which subsided after a few minutes, and there resulted a deep orange-red liquid. On adding water a yellow oil was precipitated, which, on repeatedly being washed with water and kneaded with a glass rod, became viscous and finally solidified. It was purified by crystallizing from hot alcohol, from which it is deposited in radial aggregations of fine needles. Fuming nitric acid produces the same result, as was shown by the crystalline form, melting-point and analysis for nitrogen, but it acts more readily. Action began at  $60^\circ$  and rose of its own accord to  $75^\circ$ .

This dinitromethylphenylether is a very yellow compound which dyes the hands and paper yellow. Its alcoholic solution is intensely yellow, and when agitated with water colors it distinctly yellow. It has a slightly bitter taste, and melts at  $101^{\circ}$ . The mode of formation as well as the analysis for nitrogen would point to its being a dinitromethylphenylether. Found, 10.42 per cent. N; calculated, 10.22 per cent.

NITRO-2-NITRO-2'-METHYL PHENYLETHER.

This was prepared in the same manner as the preceding compound, from the corresponding nitromethylphenylether. It is a sulphur-yellow compound which crystallizes from hot alcohol in well-defined crystals that have very much the same appearance as those of 2-nitro-4'-methyl phenylether. It melts at  $98^{\circ}$ . An analysis for nitrogen gave 10.42 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-4'-METHYL PHENYLETHER.

This was prepared by the same method as its analogues. It is light yellow in color and changes to a brownish hue on exposure to light. It was purified by crystallizing from alcohol and melts at  $100^{\circ}$ . An analysis for nitrogen gave 9.95 per cent.; calculated, 10.22 per cent.

NITRO-2-NITRO-3'-METHYL PHENYLETHER.

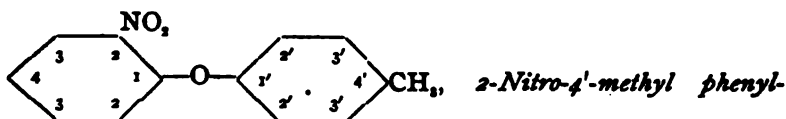
This substance was prepared from the corresponding nitromethylphenylether by the same method as its isomers that have been described. It is yellow and crystallizes from alcohol in radial aggregations of thin plates, which melt at  $106^{\circ}$ . An accident befell the analysis for nitrogen and there was not enough of the substance at hand to repeat it, but, judging from the fact that the other nitromethylphenylethers have yielded a dinitro derivative under the same conditions, it would seem likely that this is also a dinitromethylphenylether.

HEXANITRO METHYL PHENYLETHER,  $(\text{NO}_2)_6.\text{CH}_2.\text{C}_6\text{H}_4.\text{O}$ .

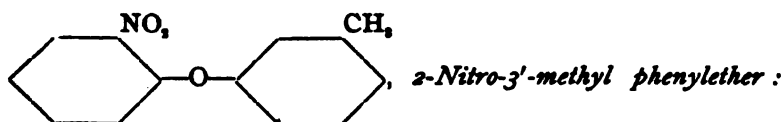
4-Nitro-4'-methyl phenylether was boiled with strong nitric acid for three-fourths of an hour. When the solution was poured into cold water a light yellow oil was precipitated which quickly

solidified. It was purified by crystallization from hot alcohol in which it is very soluble. It is also soluble in benzene, ether, and acetic acid, and sparingly soluble in water. It deflagrates like a nitrate when ignited in the flame of a lamp. Two analyses for nitrogen gave 18.15 and 18.88 per cent. N; calculated, 18.55 per cent.

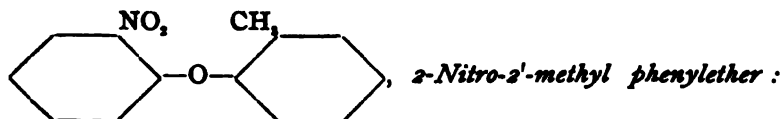
For the sake of greater clearness in comparison the graphic formulas of the six isomeric nitromethylphenylethers are given here:



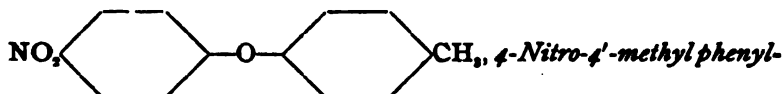
*ether* : melting-point,  $49^{\circ}$  ; free amino derivative unstable when moist.



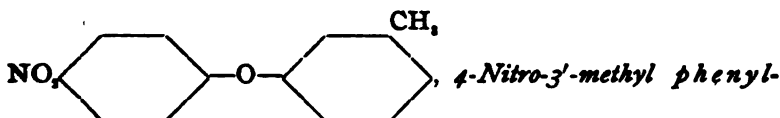
liquid ; free amino derivative very unstable when moist.



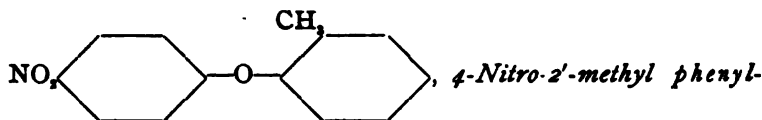
liquid ; free amino derivative very unstable when moist.



*ether* : melting-point,  $66^{\circ}$  ; free amino derivative perfectly stable when moist.



*ether* : melting-point,  $61^{\circ}$ – $62^{\circ}$  ; free amino derivative decomposes slightly when moist.



*ether*: liquid; free amino derivative partially decomposes when moist.

Three of the six isomers are liquids and three are solids. It will be observed that the nearer the nitro and methyl groups are together the greater is the tendency to be a liquid. Of the two intermediate compounds, 4-nitro-2'-methyl phenylether and 2-nitro-4'-methyl phenylether, one is a liquid and one is a solid.

The stability of the free amino derivatives was in proportion to the distance the methyl and amino radicals were apart. The free amino derivative, 4-nitro-4'-methyl phenylether, where the two groups are as far apart as possible, was found to be the most stable. It remained in contact with water for some time without showing any signs of decomposition. 2-Nitro-2'-methyl phenylether and 2-nitro-3'-methyl phenylether where the two groups are as near together as possible are the least stable. They decomposed within a few minutes after being liberated. 2-Nitro-4'-methyl phenylether, where the two groups are one stage further apart, was a little more stable, but it decomposed before it could be dried. The two remaining compounds decomposed only partially while being desiccated.

All of the solid mother-substances are yellow and the liquids are brownish red, due to the presence of the nitro group. Phenylether described by Hoffmeister,<sup>1</sup> and also jointly by Gladstone and Tribe,<sup>2</sup> is a colorless substance. So also are ortho-, meta-, and paracresyl ethers described by the latter chemists.<sup>3</sup>

All of the nitro phenylethers that were examined decomposed when boiled under ordinary atmospheric pressure but distilled unchanged in a good vacuum. This would seem to be due to the oxidizing action of the nitro group, since the original phenylether described by Hoffmeister as well as the ditolyl ethers described by Gladstone and Tribe distil unchanged under ordinary atmospheric pressure. The nitromethyl phenylethers

<sup>1</sup> *Ber. d. chem. Ges.*, 3, 748.

<sup>2</sup> *J. Chem. Soc.* (1882), p. 6.

<sup>3</sup> *Ibid.*, (1886), p. 25.



with the nitro group in the para position were not examined in this regard but it is quite possible that they would distil under ordinary atmospheric pressure unchanged. Paranitro phenylether described by Haeussermann and Teichmann<sup>1</sup> distilled unchanged at 320°. The boiling-points under diminished pressure lie quite close together, varying from 196° under a pressure of 30 mm. in case of 2-nitro-2'-methyl phenylether to 230°-233° under a pressure of 30 mm. in case of 4-nitro-3'-methyl phenylether.

All are darkened on exposure to light, but not in the same degree. 4-Nitro-4'-methyl ether seems to be the most sensitive to light.

According to Hoffmeister, chromic acid in acetic acid solution does not affect diphenylether on long-continued heating but I have found that it attacks all of the nitro methyl phenylethers in my hands. 2-Nitro-4'-methyl phenylether, however, first yielded a carboxyl acid by oxidation of the side-chain. Repeated attempts to obtain carboxyl acids with the other isomers were not successful.

All yield a monosulphonic acid derivative by warming with concentrated sulphuric acid on the water-bath. The nitromethylphenylethers differ from phenylether in that, as Hoffmeister found, it yielded a disulphonic acid derivative. They were similar in that they seemed to be capable of existing in two modifications. When a solution of one of the sulphonic acid derivatives is evaporated to a small bulk on the water-bath a thick syrupy liquid separates which is of a deep yellow or red color. (This was at first thought to be possibly due to the action of nitric acid, introduced by the addition of lead nitrate to precipitate the excess of sulphuric acid, but lead chloride was substituted with the same result.) If this is dissolved in hot water and allowed to stand, it deposits white or light yellow crystals which, in every case where the determination was made, melted above 100°. None of them were found to be deliquescent as Hoffmeister found his disulphonic acid derivative to be, but one was hygroscopic after desiccation over sulphuric acid. The sulphonic acid of 2-nitro-2'-methyl phenylether, which was the first derivative prepared, and

<sup>1</sup> *Ber. d. chem. Ges.*, 39, 1446.

which was reported in a previous paper, was obtained only in the syrupy form, but in view of what has been observed since with regard to its isomers, it is very probable that it would also have crystallized, if similar conditions had been supplied. Seven out of ten salts that were analyzed were found to contain water of crystallization, varying from 1 to 4 molecules. Water solutions of all of the acids and salts were more or less yellow whether the acids and salts themselves were yellow or not.

Orthobromnitrobenzene seems to act the most readily upon the potassium cresolates. Parabromnitrobenzene and the potassium cresolates require a continued application of heat for a longer or shorter period.

The specific gravities of 2-nitro-2'-methyl phenylether and 2-nitro-3'-methyl phenylether are about 8.5 per cent. higher than those of diphenylether and ditolyl ether as determined by Gladstone and Tribe and considerably less than that of paranitrophenylether as determined by Haeussermann and Teichman.<sup>1</sup>

There is a marked tendency to crystallize in radial aggregations or warty masses. This property is especially noticeable in the salts of the sulphonic acid derivatives. It was first noted in the barium salt of the disulphonic acid derivative of phenylether, by Hoffmeister.

All yielded a dinitro derivative with great readiness by simply heating with concentrated nitric acid, when they passed into solution. It is possible that some of these substances are identical, since their melting-points, as determined, lie quite close together, *e. g.*, nitro-2-nitro-4'-methyl phenylether, with a melting-point of 100°, and nitro-4-nitro-4'-methyl phenylether, with a melting-point of 101°. Only one of the mother-substances was boiled with concentrated nitric acid for any length of time. It yielded a hexanitro derivative.

Other work is contemplated for the coming year on two or three lines to extend our knowledge of phenylether and its derivatives.

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STOUX CITY, IOWA,  
August 30, 1902.

<sup>1</sup> *Ber. d. chem. Ges.*, 29, 1448.

# AN INVESTIGATION OF AMMONIO-SILVER COMPOUNDS IN SOLUTION.

BY W. R. WHITNEY AND A. C. MELCHER.

Received October 9, 1902.

## I. INTRODUCTION.

This investigation was begun and in large part executed nearly three years ago at a time when much uncertainty existed in regard to the constitution of the ammonio-silver compounds in solution. Its completion and publication was, however, unavoidably delayed, and in the meantime other investigations have been published, which leave no reasonable doubt that these compounds have the formula  $(\text{Ag}(\text{NH}_3)_2)\cdot\text{Cl}$ , etc., the silver existing in dilute solution almost wholly in the form of the complex cation  $\text{Ag}(\text{NH}_3)_2^+$ . This conclusion is confirmed by experiments based on a variety of different principles. Reychler<sup>1</sup> showed that the freezing-point of silver nitrate or sulphate solution is almost unaffected by the addition of ammonia until 2 mols have been added for each atomic weight of silver present, and that subsequent additions then produce the normal lowering, the same as in pure water. Konowalow<sup>2</sup> and Gaus<sup>3</sup> found that silver nitrate and chloride added to a solution of ammonia reduced the partial pressure of the ammonia gas to a value equal to that of a solution of pure ammonia of a concentration less by 2 mols of ammonia for each atomic weight of silver present. Berthelot and Delepine<sup>4</sup> proved by mixing dilute silver nitrate and ammonia solutions that no heat effect resulted upon adding either compound in excess of the amount corresponding to the ratio  $1\text{AgNO}_3:2\text{NH}_3$ . Finally Bodländer and Fittig<sup>5</sup> have made a thorough investigation of the solubility of silver chloride and bromide in ammonia solutions of various concentrations and that of the former salt in solutions containing both ammonia and potassium chloride or ammonia and silver nitrate, and by application of the Mass Action Law to the results have shown that the silver is present almost exclusively in the form of the compound  $\text{Ag}(\text{NH}_3)_2^+\cdot\text{R}^-$  and its ions. They also

<sup>1</sup> *Ber. d. chem. Ges.*, 28, 555 (1895).

<sup>2</sup> *Ztschr. phys. Chem.*, 28, 558 (1898).

<sup>3</sup> *Ztschr. anorg. Chem.*, 28, 236 (1900).

<sup>4</sup> *Compt. Rend.*, 129, 326 (1899).

<sup>5</sup> *Ztschr. phys. Chem.*, 39, 597 (1901).

confirmed this conclusion by measuring the electromotive force of concentration elements composed of silver electrodes in two solutions containing the same concentration of silver nitrate or chloride and different concentrations of ammonia, or the reverse. From both the solubility and electromotive force values they derived the dissociation-constant of the complex ion with reference to its components ( $\text{Ag}$  and  $\text{NH}_3$ ), and found it to be extremely small.

In spite of these numerous investigations on the subject, it has seemed to us that our own experiments were worthy of publication; first, because they furnish further evidence of the formation of the ion  $\text{Ag}(\text{NH}_3)_2^+$  by an entirely independent method—that of electrical transference; second, because many of the experiments involving principles previously applied were made with silver hydroxide instead of with silver salts, so that the data are new ones; and third, because, even when the same compounds and methods were used the confirmation of quantitative data by independent investigators is always of some value.

## II. TRANSFERENCE EXPERIMENTS.

Since the conductivity and dissociation of ammonium hydroxide is very slight, and that of the silver and ammonio-silver compounds is comparable with that of other salts, the simple or complex silver ions will alone migrate to an appreciable extent when a solution containing both ammonia and silver salt is electrolyzed. If, therefore, such a solution is placed at the anode end of an electrolysis tube, the rest of which is filled with some other electrolyte (like sodium nitrate), and a current is passed through, and if after a sufficient time the ratio of silver to ammonia is analytically determined in the adjoining and more remote portions of the solution which originally contained neither of these substances, the composition of the complex ion can be determined, provided that only a single kind is formed, and that this does not undergo a considerable dissociation in the absence of its dissociation products.

Experiments of this nature have been made by us on ammonio-silver nitrate and sulphate, with solutions of each salt having two different ratios of ammonia to silver in the anode part of the tube. The apparatus used in these experiments has been previously

described by A. A. Noyes.<sup>1</sup> It consists of two large glass U-tubes which have one of their arms bent at right angles and which are joined beyond the bends by a piece of soft rubber tubing. The inside arms were completely filled, and the outside arms were charged for about 1 cm. in one tube and 4 cm. in the other tube above the top of the lower bends, with a solution of the sodium salt, nitrate or sulphate, having a concentration of one-tenth mol per liter. On the side having the least solution, about 50 cc. of an ammonio-silver solution of known ratio of ammonia to silver and of a concentration in ammonia of 1 mol per liter was now added; and this, owing to its greater specific gravity, immediately sank into the bend. Methyl orange, which had been previously added to the ammonio-silver solution to color it yellow, showed the line of demarkation between the sodium salt solution and the ammonio-silver salt solution and served to give an indication of any possible stirring during the electrolysis. In the case of the nitrate, nitric acid and ammonia were added to the cathode and anode sides respectively, as the electrolysis proceeded, to neutralize the products of the electrolysis, while with the sulphate enough sulphuric acid and ammonia were added at first to neutralize all products which might be formed. Both of these methods of neutralizing the products of electrolysis were tested by electrolyzing a sodium salt solution alone, without the addition of the ammonio-silver solution; in these tests in the arm adjoining the anode the portions were found to remain entirely neutral. When after five hours the electrolysis was stopped, the portions numbered 1-3 were taken from the inside arm beginning Portion 1 about 1 cm. above the line of demarkation. These were analyzed by first titrating the ammonia with nitric acid and then precipitating the silver as chloride, filtering on Gooch crucibles and weighing after drying at 150°. The experimental data are given in Tables I and II. The ratios of the ammonia to silver are expressed in equivalents. The temperature was 25° in all cases. The current used was between 0.15 and 0.20 ampere.

<sup>1</sup> This Journal, 23, 42 (1901).

TABLE I.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER NITRATE.

Expt. No.	Initial ratio $\text{CNH}_3 : \text{Cag}$ at anode.	Portion No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.4625 N $\text{HNO}_3$ used.	Ratio $\text{CNH}_3 : \text{Cag}$ .
1	2.5	1	50	0.5729	17.84	2.065
		2	50	0.5517	17.06	2.051
		3	54	0.3062	9.27	2.008
2	2.5	1	45	0.4784	14.85	2.059
		2	57	0.5921	18.27	2.046
		3	71	0.4850	14.93	2.042
3	3.5	1	40	0.3873	11.99	2.052
		2	48	0.4193	12.79	2.023
		3	61	0.2003	6.19	2.054
4	3.5	1	45	0.4613	14.59	2.097
		2	49	0.5016	15.85	2.096
		3	61	0.4929	15.48	2.082
5	3.5	1	38	0.3990	12.48	2.074
		2	49	0.4882	15.29	2.077
		3	57	0.3722	11.57	2.062

TABLE II.—TRANSFERENCE EXPERIMENTS WITH AMMONIO-SILVER SULPHATE.

Expt. No.	Initial ratio $\text{CNH}_3 : \text{Cag}$ at anode.	Portion No.	Weight of portion.	Weight of AgCl obtained.	Cc. 0.2006 N $\text{HNO}_3$ used.	Ratio $\text{CNH}_3 : \text{Cag}$ .
1	2.5	1	41	0.5065	37.34	2.121
		2	67	0.4862	34.47	2.040
		3	68	0.1034	7.24	2.015
2	2.5	1	41	0.4032	29.57	2.110
		2	59	0.5485	38.44	2.017
		3	68	0.1637	11.29	1.985
3	2.5	1	56	0.5173	37.32	2.075
		2	58	0.4065	28.10	1.989
		3	74	0.0414	2.81	1.95
4	3.5	1	49	0.1700	13.83	2.289
		2	48	0.1377	10.78	2.258
		3	67	0.0616	4.46	2.083
5	3.5	1	45	0.2352	19.91	2.435
		2	44	0.2032	14.95	2.117
		3	62	0.0631	4.47	2.038
6	3.5	1	65	0.5041	40.92	2.335
		2	57	0.3976	29.32	2.121
		3	69	0.0757	5.57	2.117

The atomic ratio of ammonia to silver in each experiment with the ammonio-silver nitrate is almost the same in all portions, but it does have a slightly larger value in the portion nearest the

ammonio-silver solution at the anode. This mean value of the ratio is 2.045 when the original ratio is 2.5, and 2.069 when it is 3.5.

The atomic ratio in the experiments with ammonio-silver sulphate is always higher in the portion adjoining the anode portion than in the more remote ones and considerably larger than 2.0. It is doubtful whether this has any significance, however, for that portion may have been influenced mechanically by the anode portion. The mean value of the ratio in Portions 2 and 3 is 2.000 in the experiments where the original ratio at the anode was 2.5, and 2.122 in those where that ratio was 3.5.

It is evident from all these results that the ammonio-silver ion must have the formula  $\text{Ag}_n(\text{NH}_3)_n$ . This is therefore a confirmation of the conclusion drawn from the results by other methods. These experiments furnish, of course, no indication as to the value of  $n$  in the formula.

### III. FREEZING-POINTS OF SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

The silver oxide, used in the freezing-point and conductivity experiments, was prepared from clear crystals of silver nitrate and chlorine-free potassium hydroxide. It was precipitated from boiling solution and washed with boiling water. Its freedom from silver chloride was proved by dissolving it in nitric acid and subsequently diluting. The ammonia used was made by diluting the commercial chemically pure ammonia of specific gravity 0.90.

The freezing-point determinations were made with the Beckmann apparatus, the usual precautions with reference to the quantity of ice separated and the temperature of the outer bath being observed. The solutions used in the experiments numbered 1-15 in the following table were obtained by saturating ammonia solutions of various concentrations with silver oxide at 25°; the analytical data in regard to them will be found in Table V under the section on Solubility Experiments. The solutions used in the experiments numbered 21 and 22 were not saturated, and were prepared especially for the freezing-point work.

The first column in the table gives the experiment numbers, which correspond to those in Table V. The second and third

columns contain the concentrations in mols of silver and ammonia per 1000 grams of water, calculated on the assumption that the silver exists as  $\text{Ag}(\text{NH}_3)_2\text{OH}$  and the remaining ammonia as  $\text{NH}_4\text{OH}$ . The fourth column contains the actual freezing-point of the ammonio-silver solution, while in the fifth column is the freezing-point of the ammonia solution of equivalent concentration, calculated with the constant, 18.6. The rise in freezing-point caused by the addition of silver oxide is given in column 6; and the corresponding decrease in the number of mols present, calculated by using 18.6 as the molecular lowering, is given in column 7.

TABLE III.—FREEZING-POINTS OF AQUEOUS SOLUTIONS OF SILVER HYDROXIDE AND AMMONIA.

Experi- ment No.	Mols AgOH per liter.	Mols $\text{NH}_3$ per liter.	Freezing-points.		Difference.	Decrease of mols present.
			Ammonio- silver solution.	Pure ammonia solution.		
1	0.0654	0.214	0.378	0.395	0.017	0.009
2	0.0658	0.220	0.388	0.407	0.019	0.010
3	0.134	0.458	0.838	0.846	0.008	0.004
4	0.140	0.469	0.856	0.866	0.010	0.005
5	0.205	0.671	1.228	1.238	0.010	0.005
6	0.205	0.684	1.244	1.261	0.017	0.009
9	0.251	0.811	1.460	1.496	0.036	0.019
10	0.248	0.827	1.506	1.527	0.021	0.011
11	0.242	0.830	1.500	1.531	0.031	0.017
12	0.257	0.876	1.588	1.616	0.028	0.015
13	0.278	0.899	1.616	1.659	0.043	0.023
15	0.299	0.999	1.820	1.843	0.023	0.012
21	0.111 <sup>1</sup>	0.405 <sup>1</sup>	0.734	0.748	0.014	0.008
22	0.151 <sup>2</sup>	1.063 <sup>2</sup>	1.948	1.964	0.016	0.009

A consideration of the magnitude of the values given in column 6 shows that the freezing-point is only very slightly raised even by the addition of considerable quantities of silver oxide. A comparison of columns 3 and 7 shows that the number of molecules, which have disappeared on the addition of silver hydroxide is only, in the extreme case, 4 per cent. of the total number of molecules present. This change is so small that the number of

<sup>1</sup> Ten grams of this solution required 10.67 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 0.1354 gram of silver chloride.

<sup>2</sup> Fifty grams of this solution required 122.71 cc. of 0.4715 normal hydrochloric acid for its neutralization and yielded 1.0394 grams of silver chloride.



molecules may be said to be unchanged by the solution of silver oxide in the solution. It is evident that this fact is consistent with the formation of the compound  $\text{Ag}(\text{NH}_3)_2\text{OH}$  only under the assumption that the dissociation of this compound is substantially complete. In that case for every 2 molecules of ammonia which disappear, 2 new molecules,  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{OH}^-$ , are formed. As there were no existing data on the conductivity of ammonio-silver hydroxide, we have investigated it in this direction.

#### IV. CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

The saturated solution of Experiment 15 (Tables III and V) and four dilutions of it made outside of the resistance cell by means of graduated flasks were used for the conductivity measurements. The ratio  $\text{NH}_3:\text{Ag}$  in this solution was 3.35. As the ammonio-silver hydroxide proved to be a highly dissociated base, the excess of ammonia could have, in its presence, no appreciable conductivity of its own, and it served to reduce any tendency of the complex ion to dissociate into its components. The measurements were made by the usual method of Kohlrausch at a temperature of  $24.75^\circ$ . The conductivities are expressed in reciprocal ohms. The cell-constant determined by means of  $1/_{50}$  molar potassium chloride was 954.8. The results are presented in the following table.

TABLE IV.—EQUIVALENT CONDUCTIVITY OF AMMONIO-SILVER HYDROXIDE.

Liters per mol.	Actual conductivity.	Equivalent conductivity.
3.35	0.0610	194.8
6.69	0.0314	200.5
13.38	0.0159	203.3
26.75	0.00804	205.3
53.50	0.00403	205.8

The equivalent conductivity of completely dissociated silver hydroxide is at this temperature, according to Kohlrausch's values for the separate ion, 258.5.<sup>1</sup> This value is of the same order of magnitude as those given in the table, and it proves that the ammonio-silver hydroxide unlike ammonium hydroxide is a largely dissociated base. This conclusion is further confirmed by the fact that its equivalent conductivity changes only very slightly with increasing dilution. The difference between its value in

<sup>1</sup> See *Sitzungsber. kön. preuss. Akad. der Wissenschaft*, (1901), p. 1031.

$1/33.5$  molar solution and that of completely dissociated silver hydroxide may well be wholly due to the slower rate of migration of the complex ion and to the usual small proportion of undissociated molecules present at such concentrations even in the case of highly dissociated bases like potassium hydroxide.

The facts that this complex base is nearly completely dissociated and that the freezing-point of ammonia solutions does not change on dissolving silver hydroxide in them show that the composition of the complex compound must be represented by the formula  $\text{Ag}_n(\text{NH}_3)_{n+1}(\text{OH})_n$ ; for when  $(n+1)$  molecules of  $\text{NH}_4\text{OH}$  disappear through combination, this formula evidently requires that  $(n+1)$  be reproduced, namely  $n$  molecules of  $\text{OH}'$  and 1 molecule of  $\text{Ag}_n(\text{NH}_3)_{n+1}$ .

#### V. SOLUBILITY OF SILVER OXIDE, CHLORIDE, AND BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

The silver oxide was prepared as described in Section 3. The silver chloride was prepared in a dark room from silver nitrate crystals by precipitation with potassium chloride, which had been previously twice crystallized from hot water. It was then washed free from chlorides. The silver bromide was made from potassium bromide, which had been boiled for half an hour with bromine to expel all iodine and then crystallized from solution. After washing it free from soluble bromides, it was rotated in a bottle with two successive portions of half-normal ammonia to dissolve any chloride present. The ammonia was made by the distillation from potassium hydroxide of commercial ammonia.

The solutions were saturated by rotating them for six hours or more in the solubility apparatus described by Noyes,<sup>1</sup> the temperature of the bath being kept constant within  $0.05^\circ$ . In the cases of the silver chloride and bromide experiments, the state of saturation was approached both from the undersaturated and the supersaturated side, the two procedures being distinguished by the letters  $u$  and  $s$  in the tables below. Since the solubility is greater the lower the temperature, in the former procedure the silver compound was added to the ammonia solution only after it had been brought to the temperature of the bath; in the latter, the solutions were first shaken at  $18^\circ$  for fifteen minutes with an

<sup>1</sup> *Ztschr. phys. Chem.*, 9, 606 (1892).

excess of the salt and then rotated in the thermostat. In the case of silver oxide, the oxide was added to the ammonia at room temperature and then immediately placed in the thermostat for rotation. The experiments were all made at  $25^{\circ}$ , except that two were made with silver oxide at  $0^{\circ}$  for the purpose of orientation.

The results are given in Tables V to VII, which are sufficiently explained by the headings.

It will be seen that in the experiments with silver oxide the ratio  $C_{\text{NH}_3} : C_{\text{Ag}}$  is constant within the experimental error throughout the whole range of concentration, even though that of the ammonia varied from about 0.2 to 1.5 molar. In other words, within these limits of concentration the quantity of silver dissolved is almost exactly proportional to the quantity of ammonia in the solution. It has already been shown by Bodländer and Fittig<sup>1</sup> that, assuming the complex compound to be completely dissociated into its two ions, this constancy of the ratio is predicted by the Mass Action Law for any compound of the formula  $\text{Ag}_n(\text{NH}_3)_n + \text{R}_n$  and only for one of that formula. As the conductivity measurements of Table IV show that the undissociated portion is relatively small, this constant ratio shows beyond a doubt that the compound in question has this general formula.<sup>2</sup> The mean value of the ratio is 3.314.

In the case of the silver chloride the ratio  $C_{\text{NH}_3} : C_{\text{Ag}}$  varies continuously in value from 13.5 when the ammonia is 2.0 molar to 20.0 when it is 0.028 molar. However, as the solution becomes more and more dilute the values become more nearly constant; and by plotting them a limiting value of 20.20 for the ratio in very dilute solution was obtained.

These results agree fairly well with those of Bodländer and Fittig, who found for 0.1 molar ammonia the ratio 19.7 (our

<sup>1</sup> *Ztschr. phys. Chem.*, 29, 598.

<sup>2</sup> It is true, to be sure, that the constancy of the ratio  $C_{\text{NH}_3} : C_{\text{Ag}}$  is much more perfect than would be expected theoretically; for a few per cent. of the undissociated compound must be present even in the most dilute saturated solution, and the absolute quantity of this should increase proportionally to the  $(n+1)$  power (instead of the first power) of the concentration of the free ammonia, and thus diminish the value of the ratio. That it does not do so is probably to be attributed partly to the same cause, whatever it may be, that makes strong electrolytes deviate in the same sense from the theoretical dilution law. It may be due in part to a compensation of the theoretical solubility increase by a decrease in solvent power in the more concentrated solutions. How considerable this last may be is shown by the experiments of Konowalow (*Ztschr. phys. Chem.*, 38, 376) and of Rothmund and Wilmore (*Ibid.*, 41, 619).

TABLE V.—SOLUBILITY OF SILVER OXIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4715 N HCl used.	C <sub>Ag</sub> = atomic weights of silver per liter.	C <sub>NH<sub>3</sub></sub> = mols NH <sub>3</sub> (total) per liter.	Ratio CNH <sub>3</sub> : C <sub>Ag</sub> .
1	9.18	0.0850	5.37	0.0654	0.214	3.272
2	9.87	0.0917	5.90	0.0658	0.220	3.351
3	10.04	0.1877	12.26	0.134	0.458	3.420
4	9.99	0.1943	12.53	0.140	0.469	3.361
5	10.09	0.2847	18.00	0.205	0.671	3.275
6	9.97	0.2807	18.03	0.205	0.684	3.343
7	14.66	0.4531	28.11	0.225	0.720	3.196
8	13.15	0.4049	25.54	0.224	0.733	3.264
9	10.10	0.3462	21.68	0.251	0.811	3.236
10	10.14	0.3432	22.41	0.248	0.827	3.336
11	14.25	0.4717	30.84	0.242	0.830	3.424
12	14.36	0.5025	32.80	0.257	0.876	3.402
13	10.07	0.3800	23.80	0.278	0.899	3.237
14	9.97	0.3730	23.82	0.276	0.915	3.320
15	25.48	1.0294	66.11	0.299	0.999	3.344
16	10.08	0.4640	29.80	0.343	1.147	3.343
17	10.55	0.6312	40.10	0.454	1.498	3.298
18	10.73	0.6612	41.40	0.470	1.522	3.235
19 <sup>1</sup>	....	1.0382	54.02	....	....	2.519
20 <sup>1</sup>	....	0.7894	41.39	....	....	2.545

TABLE VI.—SOLUBILITY OF SILVER CHLORIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.4625 N HNO <sub>3</sub> used.	C <sub>NH<sub>3</sub></sub> = mols NH <sub>3</sub> (total) per liter.	C <sub>Ag</sub> = atomic weights of silver per liter.	Ratio CNH <sub>3</sub> : C <sub>Ag</sub> .	Method of saturation.
1	47.81	0.9471	193.83	2.042	0.151	13.57	u
2	47.01	0.9264	188.76	2.017	0.149	13.51	u
3	48.05	0.9431	192.23	2.013	0.149	13.51	s
4	46.48	0.9026	184.10	1.991	0.147	13.51	s
5	49.24	0.4189	98.51	0.961	0.0616	15.59	u
6	47.76	0.3849	91.23	0.916	0.0583	15.71	u
7	47.69	0.3850	90.49	0.909	0.0584	15.59	u
8	47.93	0.3797	90.37	0.903	0.0572	15.78	s
9	48.71	0.3838	91.08	0.896	0.0569	15.73	s
10	49.76	0.3825	90.78	0.873	0.0555	15.73	u

<sup>1</sup> These two experiments were made at 0° instead of 25°.

Expt. No.	Weight of solution analyzed.	Weight of AgCl obtained.	Cc. of 0.465 N HNO <sub>3</sub> used.	CNH <sub>3</sub> = mols NH <sub>3</sub> (total) per liter.	C <sub>Ag</sub> = atomic weight of silver per liter.	Ratio CNH <sub>3</sub> : C <sub>Ag</sub>	Method of saturation.
11	48.63	0.3487	83.95	0.863	0.0541	15.97	s
12	49.16	0.3507	84.27	0.818	0.0514	15.93	s
13	74.52	0.2618	67.95	0.428	0.0249	17.23	s
14	76.19	0.2582	67.63	0.416	0.0240	17.37	s
15	72.02	0.2338	61.72	0.411	0.0235	17.50	s
16	74.89	0.2403	63.43	0.397	0.0227	17.51	s
17	144.6	0.2880	78.54	0.253	0.0140	18.08	s
18	141.8	0.2830	76.89	0.253	0.0140	18.02	s
19	143.7	0.2867	77.66	0.252	0.0140	17.95	s
20	142.0	0.2819	76.68	0.252	0.0139	18.04	s
21	525.8	0.4656	308.9	0.118	0.00621	18.82	s
22	529.1	0.4685	310.1	0.118	0.00621	19.04	s
23	504.7	0.4451	295.4	0.118	0.00619	19.09	s
24	515.0	0.4590	300.2	0.118	0.00625	18.82	s
25	548.6	0.2380	160.8	0.0590	0.00304	19.43	s
26	538.0	0.2287	157.6	0.0589	0.00297	19.73	s
27	551.9	0.2370	160.5	0.0585	0.00300	19.49	s
28	521.2	0.1114	74.73	0.0283	0.00149	19.31	s
29	517.8	0.1060	74.01	0.0287	0.00143	20.09	s
30	549.3	0.1115	77.96	0.0285	0.00142	20.12	s
31	518.1	0.1047	72.73	0.0282	0.00141	19.99	s

TABLE VII.—SOLUBILITY OF SILVER BROMIDE IN AQUEOUS AMMONIA SOLUTIONS.

Expt. No.	Weight of solution analyzed.	Weight of AgBr obtained.	Cc. of 0.202 N HNO <sub>3</sub> used.	CNH <sub>3</sub> = mols NH <sub>3</sub> (total) per liter.	C <sub>Ag</sub> = atomic weight of silver per liter.	Ratio CNH <sub>3</sub> : C <sub>Ag</sub>	Method of saturation.
1	605.6	0.1901	1483.0	0.450	0.00170	293.9	s
2	591.5	0.1740	1440.0	0.497	0.00159	311.9	s
3	617.9	0.1082	817.4	0.268	0.000941	284.7	s
4	616.1	0.1223	831.2	0.273	0.00107	256.2	s
5	622.3	0.0455	355.8	0.115	0.000391	294.7	s
6	625.5	0.0451	365.3	0.118	0.000386	298.3	s
7	611.9	0.0316	232.2	0.0764	0.000276	277.0	s
8	613.1	0.0303	236.8	0.0777	0.000264	294.5	s

value 19.1); for 0.5 molar, the value 18.8 (our value 17.0); for 1.0 molar, the ratio 15.8 (our value 15.5); and for 1.9 molar the ratio 14.0 (our value 13.7).

The fact that this considerable variation in the value of the ratio takes place with the chloride, while there is practically no variation with the oxide, is difficult of explanation. Since ammonium hydroxide is very slightly dissociated and both ammonio-silver hydroxide and ammonium chloride are strongly dissociated, not more than 2-3 per cent. of these latter compounds could be formed by metathesis; and this could therefore not account for the variation. The formation of undissociated ammonio-silver chloride might explain it; but it would be necessary to assume a much larger proportion of it than is usual with di-ionic salts, since the maximum concentration of the complex salt is only 0.15 molar.

In the case of silver bromide where the concentration of the dissolved silver is very small, the ratio shows no progressive variation with the concentration of the ammonia, though this varied from 0.08 to 0.45 molar. Thus for this salt the constancy required by the formula  $\text{Ag}(\text{NH}_3)_n + (\text{OH})_n$  is fulfilled. The mean value of the ratio is 288.8. Bodländer and Fittig, who carried the determinations up to a higher concentration, obtained for the ratio the constant value 321 for ammonia concentrations between 0.193 and 0.574 molar, while for 1.97 molar and for 3.02 molar, the values found were 284 and 260 respectively.

We will next compare the results obtained with the three different silver compounds. It has been shown by Bodländer and Fittig (p. 604 of their article) that, if the electrolytic dissociation is complete and the formula of the complex ion is  $\text{Ag}(\text{NH}_3)_n$ , and only in the case of this formula, will the constant ratio of dissolved silver to uncombined ammonia, that is, the ratio  $C_{\text{Ag}} : (C_{\text{NH}_3} - 2C_{\text{Ag}})$ , in the case of different silver salts, be directly proportional to the solubility of the salts in pure water. And they showed that the results with silver chloride and bromide conformed to this requirement of the theory. As we have investigated a third compound (silver oxide), it is of interest to make a similar comparison in the case of the three compounds. From our values of the ratio  $C_{\text{NH}_3} : C_{\text{Ag}}$  which are 3.314, 20.20, and 288.8 for

the oxide, chloride, and bromide, respectively, we get for the ratio  $C_{Ag} : (C_{NH_3} - 2C_{Ag})$  the values  $\frac{1}{1.314}$ ,  $\frac{1}{10.30}$ , and  $\frac{1}{203.4}$ . These ratios have been divided by one another in pairs, and the quotients are given in the column headed "ammonia solution" in the table below. The corresponding quotients for the solubilities in pure water are given in the column headed "pure water". The values of the separate solubilities which are used are for silver oxide<sup>1</sup>  $216 \times 10^{-6}$ , for silver chloride,<sup>2</sup>  $15.0 \times 10^{-6}$ , and for silver bromide,<sup>3</sup>  $0.71 \times 10^{-6}$ .

	Ammonia solution.	Pure water.
AgOH : AgCl .....	13.86	14.40
AgOH : AgBr .....	218.3	304.2
AgCl : AgBr .....	15.76	21.13

The agreement of the two values is fairly close in the case of the AgOH:AgCl ratio. In the other ratios, which involve silver bromide, the values are more discordant, owing undoubtedly mainly to an error in the value of the solubility in pure water of this very difficultly soluble salt. If, conversely, this solubility is calculated from those of the other two silver salts in pure water and the ammonia solution ratios, it is found to be  $0.99 \times 10^{-6}$  when the silver oxide is used as a basis, and  $0.95 \times 10^{-6}$  when the silver chloride is so used. The agreement is remarkably good. The mean of these values ( $0.97 \times 10^{-6}$ ) is probably nearer the truth than that obtained by the conductivity method. Bodländer and Fittig's results and calculations on the relative solubilities in ammonia of the bromide and chloride lead to the value  $0.86 \times 10^{-6}$ , if the solubility of the chloride in water is taken as  $15.0 \times 10^{-6}$ . By the conductivity measurements, Holleman (1893) found  $3.3 \times 10^{-6}$ , Kohlrausch and Rose  $2.1 \times 10^{-6}$ , and Kohlrausch and Dolazalek (1901)  $0.71 \times 10^{-6}$ . By electromotive force measurements Goodwin (1894) found  $0.66 \times 10^{-6}$  and Thiel (1900)  $0.81 \times 10^{-6}$ .

In conclusion, attention may be called to the significance of the experiments on the solubility of silver oxide in ammonia at  $0^\circ$ . The ratio  $C_{NH_3} : C_{Ag}$  was found by the two experiments recorded in Table V to have the value 2.53, which is much less than that

<sup>1</sup> Noyes and Kohr : This Journal, 24, 1146.

<sup>2</sup> Kohlrausch and Rose : *Ztschr. phys. Chem.*, 12, 242 (1893).

<sup>3</sup> Kohlrausch and Dolazalek : *Sitzungsber. kdn. preuss. Akad. der Wissenschaft* (1901), p. 1022.

(3.31) at  $25^{\circ}$ . In other words, the solubility of silver oxide in ammonia is much greater at  $0^{\circ}$  than at  $25^{\circ}$ . This might be due wholly or in part to an increase in the solubility of silver oxide in pure water with decrease of temperature: but this is not the case; for the heat of neutralization of silver oxide with dilute nitric acid is, according to Berthelot, 5,200 calories, while dissolved and completely dissociated bases give the value 13,700 calories, whence it follows that the heat of solution of silver oxide in water is attended by a large absorption of heat, and therefore that its solubility must increase with rise of temperature. The results at  $0^{\circ}$  therefore show that the complex ion  $\text{Ag}(\text{NH}_3)_2$  is very much more stable at that temperature than at  $25^{\circ}$ . This is in agreement with the fact, established by Berthelot and Delepine,<sup>1</sup> that a considerable evolution of heat occurs upon mixing dilute silver nitrate and ammonia solutions.

#### VI. SUMMARY.

It has been shown by this investigation:

(1) That, when an electric current is passed from a solution containing ammonia and silver nitrate or sulphate into an adjoining solution of a neutral sodium salt, an ion of the formula  $\text{Ag}_n(\text{NH}_3)_{n+1}$  migrates into the latter solution.

(2) That the freezing-point of ammonia solutions is not changed by dissolving silver oxide in them.

(3) That the equivalent conductivity of ammonio-silver hydroxide is of such magnitude, and changes so slowly with increasing dilution as to show that this compound is nearly completely dissociated.

(4) That it follows from the two facts last stated that ammonio-silver hydroxide has the formula  $\text{Ag}_n(\text{NH}_3)_{n+1}(\text{OH})_n$ .

(5) That the solubility at  $25^{\circ}$  of silver oxide in ammonia solutions is almost exactly proportional to the concentration of the latter between the investigated limits of 0.2 and 1.5 molar; this fact also is consistent only with the formula given in 4. The ratio of the solubility to the ammonia concentration is 1:3.31, both being expressed in equivalents.

(6) That the ratio of the solubility of silver chloride to the concentration of the ammonia decreases (from the initial value

<sup>1</sup> *Compt. Rend.*, 129, 326 (1899).



1:13.5 at 2.0 molar) as the concentration of the latter decreases, but finally attains at a moderate dilution (about 0.025 molar) a nearly constant value (1:20.2).

(7) That the solubility of silver bromide as previously found by Bodländer and Fittig is proportional to the concentration of the ammonia between the limits of 0.08 and 0.45 molar, and that the ratio has the value 1:289. The constancy of this ratio is in correspondence with the requirement of the formula  $\text{Ag} \cdot (\text{NH}_3)_n + i\text{Br}_n$ .

(8) That the ratio of the solubilities in dilute ammonia of silver oxide and chloride is the same as the ratio of their solubilities in water, as the formula  $\text{Ag}(\text{NH}_3)_n \cdot \text{R}'$  alone requires.

(9) That the solubility of silver bromide in water at  $25^\circ$ , is found to be  $0.99 \times 10^{-4}$  and  $0.95 \times 10^{-4}$  when calculated under the assumption of proportionality, from the relative solubilities in ammonia of silver bromide and oxide on the one hand and of silver bromide and chloride on the other.

(10) That the solubility of silver oxide in ammonia is much greater at  $0^\circ$  than at  $25^\circ$ , though the reverse is true of its solubility in pure water; and that this is due to a much slighter dissociation-tendency of the complex ion into its components at the lower temperature.

It is our agreeable duty at this point to express our sincere thanks to Prof. A. A. Noyes for his very considerable assistance and continual interest in this investigation.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 67.]

## THE ELECTROLYTIC ESTIMATION OF BISMUTH AND ITS SEPARATION FROM OTHER METALS.<sup>1</sup>

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### INTRODUCTION.

IN determining bismuth by the ordinary gravimetric methods many difficulties confront the analyst. These limitations led the author to give attention to the estimation of this metal in the electrolytic way.

<sup>1</sup> From the author's thesis for the degree of Ph.D., 1901.

A careful study of the literature was made and all the methods thus far proposed for the electrolytic estimation of bismuth were carefully considered. It was observed that frequent and numerous attempts had been made to determine it electrolytically. As far back as 1840 Cozzi separated bismuth together with other metals from animal fluids. In 1862 Nickels and, three years later, Luckow described methods for its qualitative detection in the presence of other metals. In 1880 Ludwig Schlucht published an important series of investigations on its behavior in electrolysis. From this time on methods for its quantitative estimation began to appear, Luckow, Smith and Classen being the first to do work in this direction. The methods that have been proposed are numerous and diverse in character.<sup>1</sup> The metal has been deposited from oxalic acid and ammoniacal citrate solutions, also from nitric acid, sulphuric acid and phosphoric acid solutions. Mixed electrolytes containing alkaline pyrophosphates, carbonates and oxalates have been employed. Vortmann recommends that the bismuth be deposited together with mercury as an amalgam. More recently Karl Wimmenauer modified the old nitric acid method by introducing glycerine and making use of a revolving anode.

No one of the methods proposed can be said to be entirely free from objection. In fact so doubtful is the successful determination of bismuth electrolytically that Classen does not deem it advisable to describe even one method in the last edition of his book, "Analysis by Electrolysis." Under the heading of bismuth, he merely states, that up to the present time it has been found impossible to precipitate bismuth quantitatively in compact, metallic form.

This lack of success is to be attributed mainly to two causes: (1) the non-obtainment of a dense adherent metallic deposit and (2) the formation of superoxide of bismuth on the anode. The very few methods for which it is claimed that these difficulties have been surmounted introduce other limitations and features quite undesirable, such as the use of very small quantities of metal,

<sup>1</sup> *Literature*.—Luckow: *Ztschr. anal. Chem.*, 19, 16; Classen and v. Reim: *Ber. d. chem. Ges.*, 14, 1622; Thomas and Smith: *Am. Chem. J.*, 8, 114; Moore: *Chem. News*, 23, 209; Smith and Knerr: *Am. Chem. J.*, 8, 206; Schlucht: *Ztschr. anal. Chem.*, 22, 492; Eliasberg: *Ber. d. chem. Ges.*, 19, 326; Brand: *Ztschr. anal. Chem.*, 28, 396; Vortmann: *Ber. d. chem. Ges.*, 24, 2749; Rüdorff: *Ztschr. angew. Chem.* (1892), p. 199; Smith and Salter: *Ztschr. energ. Chem.*, 3, 418; Smith and Moyer: *This Journal*, 15, 28; *Ibid.*, 15, 101; Kollock: *This Journal*, 1899; Wimmenauer: *Ztschr. energ. Chem.*, 27, 1.

the employment of unusual and involved apparatus and the use of solutions difficult to obtain or solutions which do not lend themselves well to the separation of bismuth from other metals. None of these methods offer any advantages over the ordinary analytical methods.

It was with the hope of overcoming these difficulties and eliminating the objectionable uncertainties which always attend the electrolytic determination of bismuth by any of the described methods that the present investigation was undertaken.

*Apparatus.*—The apparatus used in this work was that usually employed in electrolysis. As cathodes platinum dishes were used of the ordinary shape, having a cathode surface of 100 sq. cm. when containing 150 cc. of liquid. Some had polished interior surfaces, others had their interior surfaces roughened (sand-blasted). Larger dishes, having a capacity of 250 cc., and a cathode surface of 200 sq. cm., were also employed.

The anodes were of two styles, ordinary flat spirals of two turns of stout platinum wire, having an anode surface of 4.5 sq. cm. and basket anodes, having an anode surface of 60 sq. cm. The latter style of anodes has the same shape as the platinum dish which is used as the cathode and is perforated with quite a number of holes to allow free circulation of the electrolyte.

Platinum gauze electrodes were also experimented with. They were in the shape of upright cylinders 5 cm. high and 10 cm. in circumference, the anode surrounding the cathode, and each having an electrode surface of 10 sq. cm. They dipped, or rather, were immersed, into the electrolyte contained in a beaker-glass of 300 cc. capacity.

The advantages offered by gauze electrodes are, briefly, that a very uniform current density is obtained all over the electrode, and therefore a uniform deposit of metal, that the deposit entirely surrounds the wire and, therefore, cannot readily peel off, and finally, that larger currents can be employed, thus reducing the time of deposition.<sup>1</sup>

The current used in these depositions was derived from storage cells.

The heating of the electrolyte was accomplished by means of a

<sup>1</sup> Cl. Winkler: *Ber. d. chem. Ges.*, 32, 2192; also *Ztschr. anal. Chem.*, 39, 517.

very small flame of a Bunsen burner. A sheet of asbestos placed a quarter of an inch below the dish shielded it from the direct flame of the burner.

During the electrolysis the dishes were kept covered with cover-glasses having two perforations ground into them. Through one passed the connecting wire of the anode and through the other hung a thermometer which dipped into the electrolyte during the whole deposition so that the temperature could be closely watched.

#### SOLUTION.

Sulphuric acid, of all the available solutions from which to deposit the metal, seemed to offer the greatest advantages and was therefore selected. As early as 1883 Thomas and Smith<sup>1</sup> and in 1886 Smith and Knerr<sup>2</sup> worked with this electrolyte and with considerable success, but as this was before the introduction of precise measurement of current strength and voltage into electrolytic work, their conditions as to these points are not very definitely stated. In these experiments they limited themselves to the employment of small quantities of metal, which is objectionable as it increases the percentage error.

Having selected sulphuric acid, attention was first directed toward obtaining a solution of bismuth sulphate. The great insolubility of the sulphate and the strong tendency of the dissolved sulphate to form insoluble basic sulphates were difficulties not easily overcome, and the simple sulphate solution was soon abandoned as impracticable. Two determinations, however, were made from simple sulphuric acid solutions obtained as follows: a weighed quantity of bismuth oxide was dissolved in a few cubic centimeters of nitric acid and then evaporated down with concentrated sulphuric acid until fumes appeared, when it was diluted with water and electrolyzed.

In all the subsequent determinations definite volumes of a standardized nitric acid solution of bismuth were employed. The solution was made up as follows: 20 grams (approximately) of bismuth subnitrate were dissolved in 100 cc. of nitric acid (sp. gr. 1.42) and this solution diluted to 1 liter with water. The bismuth content of the solution was then ascertained by cautiously evapo-

<sup>1</sup> *Am. Chem. J.*, 5, 114.

<sup>2</sup> *Ibid.*, 8, 206.

rating 20 cc. to dryness in a porcelain crucible and igniting to bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and weighing as such. 10 cc. of such a solution will contain from 0.10 to 0.15 gram of bismuth and 1 cc. of nitric acid.

#### EXPERIMENTAL PART.

Definite volumes of the standardized bismuth solution were electrolyzed in the presence of free sulphuric acid and an alkali sulphate, the dilution being usually 150 cc.

The effect of the quantity of sulphuric acid on the deposition was studied, also the influence of different alkali sulphates in varying amounts. Further, the effect of variations in the temperature, cathode surface, current density, dilution, and the style of the electrodes received careful consideration. The quantity of nitric acid was also varied and its effect noted.

After making quite a number of experiments in the variation of the quantity of sulphuric acid, 2 cc. of acid of specific gravity 1.84 were found to give the best results. When more acid than that is used it has a solvent influence on the deposited bismuth and makes it almost impossible to precipitate the last traces of the metal.

The presence of an alkali sulphate in solution was found to be essential for obtaining good metallic deposits. In the presence of sulphuric acid alone the metal does not deposit in good form nor completely. Sodium, potassium and ammonium sulphates were experimented with; of the three, potassium sulphate yielded the best results, 1 gram being the most favorable quantity. Sodium sulphate, however, can be used and good results be obtained. In the presence of ammonium sulphate bismuth is deposited in beautiful form, but there is a tendency to superoxide deposition on the anode. Very little of the latter indeed separates, but the slightest quantity is enough to be considered objectionable. The use of ammonium sulphate is therefore not to be recommended.

Larger quantities of nitric acid than that introduced with the standard bismuth solution were found to be objectionable, causing the bismuth to come down loose and black.

It was found that the temperature has considerable influence on the character of the deposit. In the cold it is impossible to precipitate the bismuth in a compact metallic form. On the other hand, when heated to a temperature as high as  $70^\circ$  the electrolyte

exerts a solvent action on the bismuth deposited, making it difficult to completely precipitate the metal. Another objection to high temperatures is the formation of gas bubbles on the bottom of the dish. The bismuth deposits about these in loose, black, spongy masses, which readily become detached and are lost in washing the deposits. If bubbles are noticed, it is advisable to gently tap the dish with the finger, causing them to rise to the surface.

A temperature of from  $45^{\circ}$  to  $50^{\circ}$  C. was found to be the most favorable. Roughened cathode surfaces are not advantageous, the bismuth depositing better on polished surfaces.

In all the depositions it was found absolutely necessary to employ a low current strength, especially during the first part of the deposition until most of the metal was precipitated. If a current, much exceeding 0.03 ampere was used as the initial current, the bismuth invariably came down dark and loose. Experiment showed a current strength of 0.02 to 0.05 ampere, depending on the style of electrodes, to be the proper one, the voltage ranging from 1.8 to 2.0 volts. Toward the end of the deposition, when most of the metal has been deposited, the current can be increased to 0.10 to 0.15 ampere to bring down the last traces of bismuth.

The following tables contain the results of determinations made from the different electrolytes after the most favorable conditions for each had been worked out by previous experiments.

Most of the deposits obtained in these determinations were very metallic in appearance, steel-gray in color, usually having the pinkish tinge or caste so characteristic of metallic bismuth. Often the deposited metal was quite crystalline.

The following is a brief statement of the most favorable conditions:

0.10 to 0.15 gram of metal dissolved in 1 cc. of nitric acid (sp. gr. 1.42.)  
2 cc. of sulphuric acid (sp. gr. 1.84.)  
1 gram of potassium sulphate.  
150 cc. total dilution.  
Time, 8 to 9 hours.  
Temperature,  $45^{\circ}$  to  $50^{\circ}$  C.  
N.D.<sub>100</sub> = 0.02 ampere.  
Volts 1.8.

During the last hour the current strength should be increased

## BISMUTH FROM SODIUM SULFATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Grams.	Dilution. Cc.	Temperature. °C.	Time. Hours.	N.D. or Ampere.	Voltage. Volts.	Style of cathode.	Character of the deposit.
0.1182	0.1186	2	1	125	50	7½	0.03	1.7	smooth	steel-gray, pink tinge.
0.1182	0.1177	3	1	125	52	7	0.03	1.7	"	"
0.1182	0.1190	2	1	125	51	5	0.025	1.7	"	light gray, few black spots.
0.1182	0.1184	2	1	125	55	6½	0.025	1.8	"	same
0.1182	0.1186	2	1	125	43	7	0.02	1.7	"	very light and metallic.
0.1182	0.1177	2	1	125	50	7	0.02	1.7	rough	light gray and metallic.
0.1182	0.1178	2	1	125	45	7½	0.02	1.7	smooth	" " with few spots.
0.1182	0.1179	3	1	125	53	6½	0.02	1.7	"	" " with pink tinge.
0.1182	0.1186	2	1	125	53	7	0.02	1.8	rough	"
0.1182	0.1193	2	1	125	60	8	0.02	1.8	smooth	" " metallic.
0.1182	0.1180	3	1	125	55	7	0.02	1.7	rough	" " "
0.1182	0.1180	2	1	125	52	8	0.02	1.8	smooth	" " "
0.1182	0.1181	4	1	..	60	8½	0.02	1.7	"	" " "
0.1182	0.1184	4	2	125	66	24	0.02	2.0	"	" " crystalline.
0.1182	0.1186	2	1	125	60	8	0.02	1.8	"	" " "
0.1182	0.1180	2	1	125	50	..	0.02	2.0	"	" " metallic.
0.1182	0.1181	2	1	150	45	8	0.02	1.8	"	" " "
0.1182	0.1180	2	1	150	45	7½	0.02	1.8	"	" " "
0.1182	0.1181	2	1	200	..	..	0.02	..	"	" " "
0.0591	0.0590	2	1	150	45	24	0.02	1.9	"	" " metallic.
0.1182	0.1179	2	2	125	..	7½	0.02	1.7	rough	" " "
0.1182	0.1188	2	1	125	60	7	0.02	1.8	"	" " "
0.1182	0.1186	2	1	125	62	7	0.02	2.0	"	" " crystalline.
0.1182	0.1180	2	1	125	50	..	0.02	2.0	smooth	" " "
0.1182	0.1176	1	1	125	60	7½	0.02	1.7	"	" " "
0.1434	0.1433	2	1	150	45	22	0.02	2.0	"	dark gray.
0.1434	0.1438	2	1	150	45	9½	0.02	1.8	"	light gray.
0.1434	0.1438	2	1	150	45	18	0.02	1.8	"	" " "
0.1434	0.1434	2	1	150	45	24	0.02	1.8	"	rather dark.

## FROM SODIUM SULPHATE SOLUTION, USING BASKET ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. No. Ampere.	Voltage. Volta.	Character of the deposit.
0.1182	0.1187	2	1	125	6½	60	0.03	2.1	light gray, metallic.
0.1182	0.1171	2	1	125	6½	55	0.03	2.0	dark, but adherent.
0.1182	0.1176	2	1	125	7	55	0.02	1.8	dark gray.
0.1434	0.1436	2	1	150	22	45	0.02	1.8	light and metallic.
0.1434	0.1436	2	1	150	20	45	0.02	1.8	good, but a little dark.
0.1434	0.1431	2	1	150	18	45	0.02	1.8	light gray.

## FROM SODIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. No. Ampere.	Voltage. Volta.	Character of the deposit.
0.1182	0.1181	2	1	200	24	45	0.03	2.0	light gray.
0.1434	0.1433	2	1	200	7	45	0.03	2.0	" " very metallic.
0.1434	0.1434	2	1	200	9½	45	0.03	2.0	" " "
0.1434	0.1433	2	1	200	8½	45	0.03	2.0	" " "

## FROM POTASSIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. No. Ampere.	Voltage. Volta.	Character of the deposit.
0.1434	0.1428	2	0.6	150	8	45	0.02	1.9	light gray.
0.1434	0.1436	2	0.6	150	9	50	0.02	1.9	" " very metallic.
0.1395	0.1400	2	1.0	250	9	45	0.025	1.9	" " "
0.1395	0.1392	2	1.0	150	6½	45	0.02	1.8	" " "
0.2790	0.2790	2	1.0	150	9	45	0.025	1.9	dark, but adherent.
0.1395*	0.1393	2	1.0	150	6	45	0.02	1.7	light gray.
0.0698*	0.0698	2	1.0	150	7	50	0.02	1.8	" " "

\* Basket anode.



## FROM POTASSIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	Current strength. Ampere.	Voltage. Volts.	Character of the deposit.
0.1395	0.1394	2	1.0	200	8	45	0.06	2	light and adherent.
0.1395	0.1394	2	1.0	200	8	45	0.04	2	" "
0.1395	0.1393	2	1.0	200	7½	50	0.05	2	dark "
0.1434	0.1435	2	0.6	200	9	50	0.03	2	light and metallic.
0.1434	0.1435	2	1.0	200	8	55	0.04	2	"
0.1434	0.1431	2	1.0	200	9	50	0.035	2	" metallic.
0.1434	0.1433	2	1.0	200	8¾	45	0.03	2	" "
0.1434	0.1430	2	1.0	200	..	45	0.03	2	" "

## FROM AMMONIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Ammonium sulphate. Grams.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. Ampere.	Voltage. Volts.	Anodes.	Character of the deposit.
0.1182	0.1186	2	1	125	7	63	0.02	1.8	discolored	light gray and metallic.
0.1182	0.1186	2	3	125	8	60	0.02	1.7	"	" "
0.1182	0.1186	2	2	125	30	..	0.02	..	"	" "
0.1182	0.1174	2	2	125	7	..	0.02	..	"	" "
0.1182	0.1186	2	1	125	8	60	0.02	1.8 not	"	" crystalline.
0.1182	0.1180	2	1	125	8	60	0.02	1.8	discolored	" "
0.1182	0.1189	2	1	125	9	60	0.02	1.8 not	"	" "
0.1182	0.1179	2	1	125	8½	55	0.02	1.8	"	light gray.

to 0.15 ampere to bring down the last traces of bismuth. When gauze electrodes are used, such as were described in an earlier part of this paper, a current strength of 0.04 ampere should be used.

Heat is absolutely essential in order to obtain light, metallic deposits. If, however, the electrolysis be conducted two and a half to three hours at  $45^{\circ}\text{C}$ ., during which time most of the metal will have been deposited, it may safely be run over night in the cold. This procedure may, in some cases, be more convenient than conducting the electrolysis eight hours during the day at  $45^{\circ}\text{C}$ .

The end of the electrolysis is ascertained by raising the level of the liquid in the dish, or by testing a few drops of the solution for bismuth with ammonium sulphide.

When the metal has all been precipitated, the deposit is washed without interrupting the current. This is done by siphoning off the acid liquid, at the same time replacing it with hot distilled water. When the liquid in the dish is free from acid, the current is interrupted and the liquid poured from the dish. The deposit is washed with a little hot water and drained. It is then rinsed with a little absolute alcohol to remove the remaining water, this treatment being followed by a little ether. Finally the dish is gently warmed over a very small flame until complete evaporation of the ether, when it is desiccated, cooled and weighed.

With a good many deposits it was noticed that the alcohol tended to lift some of the deposited metal and float it away, thus involving loss. This was remedied by substituting for the alcohol a mixture of ether (2 parts) and alcohol (1 part). Treatment with this mixture is followed by anhydrous ether as usual.

When no dehydrating agents are used and the deposit is simply dried in the air by gently warming, an oxidation of the bismuth always takes place, giving high results.

The liquid should be maintained at a constant level during the electrolysis. If the level is raised, a dark border of loosely deposited bismuth forms around the dish, the depth of the liquid added. If the cover-glasses are close-fitting, scarcely any evaporation can take place, so that it is necessary to add but very little water during the electrolysis.

If the conditions as above stated be carefully followed, a good determination can always be obtained.

The problem of the electrolytic estimation of bismuth having been satisfactorily solved, attention was next given to its separation from other metals by the same means. The results of the experimentation in this direction are embodied in what follows.

## SEPARATIONS.

(1) *Bismuth from Zinc.*—These metals can be separated with ease and precision electrolytically, from sulphuric acid solution. The bismuth comes down in a beautiful compact metallic form in every case free from zinc.

To 10 cc. of a nitric acid solution of bismuth containing 0.15 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) were added 2 cc. of sulphuric acid (sp. gr. 1.84), 0.6 gram of potassium sulphate and a quantity of zinc sulphate equivalent to 0.15 gram of zinc. The solution was then diluted with water to 150 cc. and electrolyzed with a current strength of 0.02 ampere and a voltage of 2.0. The solution was heated to 50° C. The deposition was complete in about eight hours. The same precautions previously observed as to the treatment of the deposited bismuth were of course followed here.

In the following table the results of four determinations are recorded.

## RESULTS.

Bismuth taken.	Bismuth found.	Zinc.	Sulphuric acid.	Potass'm sulphate.	Dilution.	Time.	Temperature.	N.D. no.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Cc.	Gram.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1433	0.1684	2	0.6	150	8½	50	0.025	2	basket.
0.1434	0.1430	0.1529	2	0.5	150	8	50	0.02	2	spiral.
0.1424	0.1428	0.1640	2	0.5	150	8½	50	0.025	2	basket.

(2) *Bismuth from Cadmium.*—The separation of bismuth from cadmium can also be accomplished with ease and accuracy. The conditions of the separation are very similar to those of bismuth from zinc. A quantity of cadmium oxide equivalent to 0.1500 gram of cadmium was dissolved in 2 cc. of concentrated sulphuric

very small flame of a Bunsen burner. A sheet of asbestos placed a quarter of an inch below the dish shielded it from the direct flame of the burner.

During the electrolysis the dishes were kept covered with cover-glasses having two perforations ground into them. Through one passed the connecting wire of the anode and through the other hung a thermometer which dipped into the electrolyte during the whole deposition so that the temperature could be closely watched.

#### SOLUTION.

Sulphuric acid, of all the available solutions from which to deposit the metal, seemed to offer the greatest advantages and was therefore selected. As early as 1883 Thomas and Smith<sup>1</sup> and in 1886 Smith and Kneff<sup>2</sup> worked with this electrolyte and with considerable success, but as this was before the introduction of precise measurement of current strength and voltage into electrolytic work, their conditions as to these points are not very definitely stated. In these experiments they limited themselves to the employment of small quantities of metal, which is objectionable as it increases the percentage error.

Having selected sulphuric acid, attention was first directed toward obtaining a solution of bismuth sulphate. The great insolubility of the sulphate and the strong tendency of the dissolved sulphate to form insoluble basic sulphates were difficulties not easily overcome, and the simple sulphate solution was soon abandoned as impracticable. Two determinations, however, were made from simple sulphuric acid solutions obtained as follows: a weighed quantity of bismuth oxide was dissolved in a few cubic centimeters of nitric acid and then evaporated down with concentrated sulphuric acid until fumes appeared, when it was diluted with water and electrolyzed.

In all the subsequent determinations definite volumes of a standardized nitric acid solution of bismuth were employed. The solution was made up as follows: 20 grams (approximately) of bismuth subnitrate were dissolved in 100 cc. of nitric acid (sp. gr. 1.42) and this solution diluted to 1 liter with water. The bismuth content of the solution was then ascertained by cautiously evapo-

<sup>1</sup> *Am. Chem. J.*, 5, 114.

<sup>2</sup> *Ibid.*, 8, 206.

rating 20 cc. to dryness in a porcelain crucible and igniting to bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and weighing as such. 10 cc. of such a solution will contain from 0.10 to 0.15 gram of bismuth and 1 cc. of nitric acid.

#### EXPERIMENTAL PART.

Definite volumes of the standardized bismuth solution were electrolyzed in the presence of free sulphuric acid and an alkali sulphate, the dilution being usually 150 cc.

The effect of the quantity of sulphuric acid on the deposition was studied, also the influence of different alkali sulphates in varying amounts. Further, the effect of variations in the temperature, cathode surface, current density, dilution, and the style of the electrodes received careful consideration. The quantity of nitric acid was also varied and its effect noted.

After making quite a number of experiments in the variation of the quantity of sulphuric acid, 2 cc. of acid of specific gravity 1.84 were found to give the best results. When more acid than that is used it has a solvent influence on the deposited bismuth and makes it almost impossible to precipitate the last traces of the metal.

The presence of an alkali sulphate in solution was found to be essential for obtaining good metallic deposits. In the presence of sulphuric acid alone the metal does not deposit in good form nor completely. Sodium, potassium and ammonium sulphates were experimented with; of the three, potassium sulphate yielded the best results, 1 gram being the most favorable quantity. Sodium sulphate, however, can be used and good results be obtained. In the presence of ammonium sulphate bismuth is deposited in beautiful form, but there is a tendency to superoxide deposition on the anode. Very little of the latter indeed separates, but the slightest quantity is enough to be considered objectionable. The use of ammonium sulphate is therefore not to be recommended.

Larger quantities of nitric acid than that introduced with the standard bismuth solution were found to be objectionable, causing the bismuth to come down loose and black.

It was found that the temperature has considerable influence on the character of the deposit. In the cold it is impossible to precipitate the bismuth in a compact metallic form. On the other hand, when heated to a temperature as high as  $70^\circ$  the electrolyte

## RESULTS.

Bismuth taken.	Bismuth found.	Cobalt taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. 100.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500	0.5	2	150	8½	45	0.025	2	basket.
0.1434	0.1435	0.1500	0.5	2	150	8½	45	0.025	2	spiral.
0.1434	0.1430	0.1500	0.5	2	200	8½	45	0.03	2	gauze.

(6) *Bismuth from Manganese.*—Experiment showed that by this method the separation of bismuth from manganese could be effected without difficulty. The salt of manganese used in this case was manganous sulphate. The following mode of procedure was found to be the best: To a bismuth solution containing 0.1500 gram of metal and 1 cc. of nitric acid (sp. gr. 1.42) add 3 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of manganous sulphate equivalent to 0.1500 gram of manganese. Dilute this solution to 150 cc. with water and electrolyze with a current of 0.025 ampere and 2 volts, keeping the temperature at 45° C. The bismuth will be deposited in nine hours in beautiful form free from manganese.

At first the solution assumes a dark red color due to the oxidation of some of the manganese to permanganate. After an hour or two the color begins gradually to fade away and the solution again becomes colorless. A considerable quantity of hydrated oxide of manganese deposits on the anode during the electrolysis. This deposit was always examined for bismuth but in no case was it found to contain any of this metal.

## RESULTS.

Bismuth taken.	Bismuth found.	Manganese taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. 100.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1438	0.1500	0.5	3	150	23	45	0.025	1.9	spiral.
0.1434	0.1430	0.1500	0.5	3	150	9	45	0.025	2	"
0.1434	0.1435	0.1500	0.5	3	150	9	45	0.025	2	basket.
0.1395	0.1391	0.1500	0.5	3	150	9	45	0.035	2	gauze.

(7) *Bismuth from Uranium.*—Bismuth may be separated from this metal as follows: To a bismuth solution containing 0.1500 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) add 1 gram of potassium sulphate, 2 cc. of sulphuric acid (sp. gr. 1.84) and uranium sulphate equivalent to 0.10 gram of uranium. Dilute this solution to 150 cc. with water and electrolyze with a current strength of 0.025 ampere and a voltage of 2, maintaining the temperature at 45° C. The deposition is complete in eight hours and the deposited bismuth free from uranium.

## RESULTS.

Bismuth taken.	Bismuth found.	Uranium taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. no.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere	Volts.	
0.1395	0.1394	0.1000	1	2	150		45	0.025	2.1	spiral.
0.1395	0.1395	0.1000	1	2	150	8	45	0.03	0.2	basket.
0.1395	0.1399*	0.1000	1	2	200	8	45	0.04	0.2	gauze.

(8) *Bismuth from Iron.*—The deposition of bismuth from solutions containing iron is attended with considerable difficulty. Both ferrous and ferric salts were experimented with. The iron present in the solution seems to exert an influence on the bismuth, tending to hold it in solution and prevent its deposition. Especially is this true when the salt used is a ferric salt. This tendency of bismuth to be held in solution is shown even in a more marked degree when the solution contains besides ferric alum an equal quantity of chrome alum. When this is the case, a current of 0.10 ampere will often not cause the slightest precipitation of bismuth. It was thought that this behavior of bismuth could be taken advantage of to separate other metals from it. It was hoped that the bismuth would be held back by the iron and chrome alums and such metals as mercury, copper and silver be deposited from the solution. These hopes were not realized. As soon as another metal is introduced, the condition of affairs is changed, and both the metal and the bismuth are precipitated. Deposits of silver, however, were obtained containing but very little co-

deposited bismuth. Further investigation in this direction might lead to some very interesting and valuable results.

The best conditions for the separation of bismuth from iron were found to be as follows: To the bismuth solution containing 0.15 gram of bismuth and 1 cc. of concentrated nitric acid, add 2 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of ferrous sulphate or ammonium ferric alum equivalent to 0.15 gram of iron. Dilute this solution to 150 cc. and electrolyze at a temperature of 45° C. If a ferrous salt is used, the current strength should be 0.03 ampere, but if a ferric salt is in solution a higher current strength should be employed, 0.05 ampere, the voltage in both cases being 2.0. In eight hours the deposition will be complete. The precipitated bismuth will contain no iron.

In several cases the separation was made in the presence of urea nitrate, but its addition was of no advantage. The same can be said for manganese sulphate, which was also added.

#### RESULTS.

Bismuth taken.	Bismuth found.	Iron taken.	Urea nitrate.	Potassium sulphate.	Dilution.	Sulphuric acid.	Time.	Temperature.	N. D. 100.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500 <sup>1</sup>	...	0.5	150	2	8½	50	0.025	1.5	spiral.
.....	0.1431	0.1500 <sup>1</sup>	...	0.6	150	2	7½	45	0.03	2	"
.....	0.1435	0.1500 <sup>1</sup>	...	0.5	150	2	24	45	0.03	2	"
.....	0.1430	0.1500 <sup>1</sup>	...	0.5	150	2	24	45	0.03	1.7	basket.
0.1395	0.1394	0.1500 <sup>1</sup>	0.5	0.2	150	2	8	45	0.035	2	"
.....	0.1400	0.1500 <sup>1</sup>	0.5	0.2	150	2	8	50	0.035	2	spiral.
.....	0.1393	0.1500 <sup>1</sup>	0.5	0.2	200	2	8	45	0.05	2	gauze.
.....	0.1397	0.1500 <sup>2</sup>	...	0.5	150	2	9	45	0.07	2	spiral.
.....	0.1395	0.1500 <sup>2</sup>	...	0.1	150	2	9	45	0.06	2	"
.....	0.1394	0.1500 <sup>2</sup>	...	0.1	200	2	8	45	0.06	2	gauze.
.....	0.1395	0.1500 <sup>2</sup>	3.0	0.5	150	2	9	45	0.035	2	spiral.

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<sup>1</sup> Ferrous sulphate.

<sup>2</sup> Ferric ammonium sulphate.



## THE ALKALOIDS OF ISOPYRUM AND ISOPYROINE.<sup>1</sup>

BY GEORGE BELL FRANKFORTER.

Received October 16, 1908.

THE isopyrum, so far as can be ascertained, has only once been studied chemically. Hartsen,<sup>2</sup> in a brief examination of *isopyrum thalictroides*, reported the isolation of two new alkaloids. The one he named isopyrine and the other he called pseudoisopyrine. The following is a statement of the method which he used in obtaining these two substances: The root of the *thalictroides* was extracted with water and filtered. The filtrate was evaporated almost to dryness and treated with ammonia. The precipitate thus formed, consisted of aluminum hydroxide, tannic acid and the new base, isopyrine. To remove the latter, the precipitate was dried and extracted with ether. By filtering off and evaporating the ethereal solution, the alkaloid was obtained as an amorphous powder. Nothing further was done with the substance. No attempts were made to purify it or to study its properties and no salts of any kind were made.

Pseudoisopyrine, the other alkaloid, was obtained by treating the roots with alcohol, after they had been extracted with water. The alcoholic extract was condensed by evaporation and treated with ammonia as in the case of the aqueous extract. The precipitate formed by the ammonia, was filtered off, dried and extracted with ether. On removing the excess of ether, the alkaloid crystallized out in star-shaped crystals. As in the first case, no attempt was made to purify the substance and no salts were made. The author of the above paper, while applying the above names, suggested that, quite likely, these two substances were known substances, possibly mixtures of the aconite group.

The above paper was published twenty-eight years ago and nothing has been done since that time although the plant is quite abundant in certain localities. According to Gray, isopyrum is abundant throughout the central, northwestern and southwestern states. According to MacMillan,<sup>3</sup> it is widely distributed throughout Minnesota and Iowa.

<sup>1</sup> Read before the American Association for the Advancement of Science, at Denver, 1901.

<sup>2</sup> *Chem. Centrbl.* (1872), p. 523.

<sup>3</sup> "Metaspermae of Minnesota," p. 231.

My attention was first called to the American species, *isopyrum biternatum*, by Professor MacDougal, of Bronx Park, New York, who, in studying the tubers botanically, observed certain reactions which gave evidence of the presence of a substance of unusual interest. A year later, with the assistance of students, enough material was obtained to make a preliminary examination and to prove beyond a doubt, the presence of an alkaloid. The work has been renewed recently, and enough material obtained to make a careful examination. Samples were collected at different times during the summer and examined. That gathered in the early spring contained only a small quantity of the alkaloid, while that gathered later in the summer contained a maximum amount of the alkaloid. In the early spring, the roots appear as fine fibers with only here and there a very small tuber; in midsummer, the tubers were very much larger and more abundant.

The first work done on the American species was to repeat the method given by Harsten on the *thalictroides*. The results, however, were unsatisfactory and other methods were tried and enough of the material was obtained for analysis.

#### METHOD OF EXTRACTION.

Many methods, including that of Harsten, were tried but with unsatisfactory results. The method which gave best results was as follows: The roots were cleaned, dried, and pulverized and the powder thus obtained, extracted with hydrochloric acid (1:250). The extraction was made first by heating on a water-bath for an hour and then allowing to stand for twelve hours. The acid solution was then filtered off and evaporated to about one-fifth of the original volume and refiltered. The almost clear filtrate was then treated with ammonia. The precipitate formed, which, according to Harsten should contain the alkaloid isopyrine, was saved, dried and extracted with ether. It proved to be only inorganic matter. The filtrate was then evaporated to dryness and extracted with alcohol. The alcoholic solution gave distinct alkaloidal reactions but all attempts to isolate the free base failed.

The roots were now extracted with alcohol in the presence of hydrochloric acid for several hours and filtered. The filtrate was then condensed by evaporation, treated with ammonia, and

filtered. The precipitate thus obtained, was redissolved in hydrochloric acid, reprecipitated with ammonia, and filtered. This filtrate was added to the original filtrate, evaporated to dryness, and extracted with chloroform. The chloroform solution was treated with hydrochloric acid and allowed to stand for several days. At the end of that time, crystals had formed which proved to be the hydrochloride of the alkaloid.

These crystals were removed, purified by filtering through animal charcoal and again crystallized out of water. Thus obtained, the substance was a beautiful white felt-like mass of fine crystals. It is soluble in water and alcohol but almost insoluble in ether.

Under the microscope the crystals appear as long, fine, prismatic needles. The melting-point of the pure substance was found to be  $255^{\circ}$  to  $257^{\circ}$  C. The hydrochloride formed a well-crystallized platinum double salt. It is a bright yellow, granular substance, insoluble in water but slightly soluble in alcohol. It melts at  $238^{\circ}$  C.

#### THE FREE BASE, ISOPYROINE.

The hydrochloride was dissolved in a very small quantity of dilute alcohol, and sodium hydroxide cautiously added. The white flocculent precipitate formed was filtered off and dissolved in an excess of alcohol. On slowly evaporating the alcohol, the base was reprecipitated as a white, crystalline substance. These crystals had a sharp melting-point of  $160^{\circ}$  C. On drying at  $100^{\circ}$  C., the substance lost its crystalline nature and became a light gray powder. Analyses of the dried substance gave the following results:

I. 0.1230 gram of the dried substance gave 0.2814 gram  $\text{CO}_2$ ; 0.0964 gram  $\text{H}_2\text{O}$ .

II. 0.2042 gram of the dried substance gave 0.4628 gram  $\text{CO}_2$ ; 0.1599 gram  $\text{H}_2\text{O}$ .

	Calculated for the formula, $\text{C}_{20}\text{H}_{44}\text{NO}_7$ .	I.	Found.	II.
Carbon .....	62.22	62.22		61.81
Hydrogen .....	8.51	8.70		8.69
Nitrogen .....	2.54	....		....

In view of the fact that the alkaloid in hand differs widely from

the isopyrine and pseudoisopyrine of Hartsen, the base has been called isopyroine.

ISOPYROINE METHYL IODIDE,  $C_{23}H_{46}(CH_3)NO_2I$ .

The powder was treated with methyl iodide for two hours on a water-bath with reflux condenser and at the end of that time, the substance, which at first dissolved, formed a yellow residue in the bottom of the flask. The iodide was removed and reprecipitated from an alcoholic solution with water. The substance thus formed was of a yellow color and almost insoluble in water, ether and chloroform. An iodine analysis gave the following numbers:

I. 0.2204 gram of the substance gave 0.0758 gram of silver iodide.

	Calculated for the formula, $C_{23}H_{46}(CH_3)NO_2I$ .	Found.
Iodine.....	18.62	18.8

In addition to the iodide, the chloride and the platinum double salt have been made and are in process of analysis.

## NEW BOOKS.

THE ELECTRO-PLATING AND ELECTRO-REFINING OF METALS. BY WATT AND PHILIP. New York : D. Van Nostrand Company. 680 pp. Price, \$4.50 net.

This new and revised edition of Watt's "Electro-deposition" will be most heartily welcomed by all persons interested in the art of electro-plating and electro-refining. The editor has carefully revised the original work, incorporating in it the most modern advancements in the art, and by the addition of entirely new material has expanded the volume by more than 200 pages.

Two chapters are devoted to preliminary considerations: primary and secondary batteries, and thermopiles, dynamos, the cost of electrical installations of small output for electroplating, etc., etc. A most interesting historical review of electrodeposition constitutes the third chapter, which is followed by 50 pages upon the electro-deposition of copper. Most minute and exhaustive instructions are given. These show everywhere the touch of a master-workman. Gilding also receives ample consideration. Then follow directions for the electro-deposition of

silver, nickel, iron, tin, zinc, platinum, brass, bronze, etc. The chapter on the cost of electrolytic copper refining will appeal to many who are now conducting experiments on this and other metals for commercial purposes.

Thoroughness in detail and exactness in statement of procedure characterize the book. It will prove most helpful to all who use the current for the purposes it so exhaustively treats.

EDGAR F. SMITH.

**HIGHER MATHEMATICS FOR STUDENTS OF CHEMISTRY AND PHYSICS**, with special reference to practical work. By J. W. MELLOR, D.Sc., of Owens College, Manchester, England. Longmans, Green & Co. 1902. xxi + 543 pp. Price, \$4.00.

To any one who has followed the latest development of theoretical chemistry, it is clear that the chemist of the future must be also a practical mathematician. The recent successive appearance of several volumes having as one object the application of mathematics to the scientific development of chemistry shows the general recognition of this condition.

Among all these books, none seems to the reviewer more complete or adequate than that at present under discussion. The importance of a concrete conception of mathematical expression is fully realized and continually exemplified, and the arrangement is progressive and logical. "The student of this work is supposed to possess a working knowledge of elementary algebra so far as to be able to solve a set of simple simultaneous equations, and to know the meaning of a few trigonometrical formulas."<sup>1</sup> This scanty foundation is gradually amplified and built upon until the student should find himself a master of practical calculus, and capable of integrating differential equations derived from his own experimentation. Analytical Geometry, Functions with Singular Properties, Hyperbolic Functions, Fourier's Theorem, Determinants, and the Theory of Errors all receive extended discussion. The last-mentioned subject is treated in a particularly lucid and just manner, with especial emphasis upon its limitations, which are too often ignored. At the end of the book are given a collection of useful formulas and tables of reference, including a table of natural logarithms. No space is given to vector analysis, but most chemists will not be troubled

<sup>1</sup> Prologue, p. xx.

by this omission. The emphasis throughout is laid upon that which is practically useful, and the usefulness is illustrated by actual problems taken chiefly from the modern literature of physical chemistry. In general, the book leaves little to be desired, and can be warmly recommended to the many who are in search of a guide more practical than the usual formal treatise upon pure advanced mathematics. THEODORE W. RICHARDS.

TEXT-BOOK OF ELECTROCHEMISTRY. BY SVANTE ARRHENIUS, Professor at the University of Stockholm. Translated by JOHN MCCRAE, PH.D. New York: Longmans, Green & Co. 1902. xi + 344 pp.

The first chapter deals very briefly with the many fundamental conceptions, definitions, etc., necessary to a study of the subject; but the arrangement of this matter could be improved. Polarization is here the first topic touched, and it would seem more logical to let this follow the definitions of atomic weight, of temperature, electrolysis, and other such matters, some of which in fact need not be defined in a book on electrochemistry.

The second chapter is a brief one on the early history of the subject, in which much more space is devoted to the Grotthus theory than to Faraday's facts.

The third chapter covers in a concise and clear manner the laws of gases and of their application in the case of solutions. It has, however, not been shown that van't Hoff's generalization of the gas laws to solutions applies to "all finely dispersed material." Suspensions, at least, may form an exception.

The subject of properties of solutions is then fully treated. Two pages devoted entirely to valency and entitled "Review of Results Obtained," do not seem of use.

The subject of chemical equilibrium is well treated in Chapter VI.

Following the unfortunate lead of Ostwald and of Nernst, Arrhenius considers that the identical light absorption of the various equally dilute permanganate salt solutions is proof of the dissociation theory, and leaves the reader to assume that the color of the ions is a splendid support of the theory. Any one who looks into this point carefully will find it very complicated. The depth of color of salt solutions of colored ions does not change, as does the electrolytic dissociation, with the dilution. In illustrating the

process for determining the transport number, one unfortunate sentence may bother the student a little. Potassium chloride is being electrolyzed and the author states that by analysis after the electrolysis, the increase of potassium about the cathode and of chlorine about the anode enable one to make the calculation. The disposition of the deposited chlorine and potassium should have been discussed here.

The subject of electrochemistry is treated in its widest significance so that many of the physical properties of solutions are carefully considered; therefore, the work practically covers a course on the physical chemistry of solutions as this is now understood.

Two-thirds of the book are devoted to purely electrochemical topics. The treatment of each topic is concise and the selection of topics so complete that it may safely be asserted that no other English work on this subject contains so much in so small space.

The treatment of potential differences, of surface tension, and the mercury electrometers, is well connected. Six pages are devoted to a very fair treatment of the lead accumulator. The Gretz aluminum rectifying cell is also described. Several pages are devoted to practical electrochemical analysis and to copper refining.

Chapter XVII contains brief descriptions of the Peltier and the Thomson Effects, and contains also a couple of pages on the electric arc. There then follow a dozen pages dealing in a practical way with the various classes of the electric furnace and a final discussion of the effect of silent electrical discharges.

Usually when an important discovery is mentioned in the text, an interpolated number refers the reader to the original article. In this way, about 300 original references are made available. In a book of this kind such a scheme is commendable.

Very considerable credit is due to Dr. Euler and to Dr. McCrae for the improvements on the original Swedish work, which was brought up to date and translated into German by the former, and well translated into English and improved with the literature references by the latter.

The mathematics frequently employed do not extend beyond the elements of the calculus.

Because of the breadth of field treated and the general good quality of the treatment, the book is one of the best on the subject.

W. R. WHITNEY.

**PHYSICS. TEXT-BOOK FOR SECONDARY SCHOOLS.** BY FREDERICK SLATE, Professor of Physics, University of California. New York: The Macmillan Co. 1902. xxi + 1414 pp. Price, \$2.00.

The seventeen-page preface convinces the reader that the author is preparing a book from a mind trained for teaching natural science. He has clear views as to the pedagogic functions of such a work, and is consistent even to his unwillingness to confuse the mind by pictures of things which can be actually seen in the laboratory. The preface will be instructive to the many teachers who are to read it.

About 100 pages are devoted to the properties of matter; approximately an equal quantity to heat; and the subjects of sound, light, and electricity are also quite fully treated. Besides the index, there is a list of references for collateral reading, an outline of 180 experiments, and a compilation of over 100 interesting questions. The experiments are also especially carefully selected and worded,—there are no cook-book directions. The book is a readable Physics, and is not replete with definitions for the anxious student to commit to memory. He is forced by the arrangement to think for himself. In fact, there is hardly a direct definition in the book. The author's plan is to give the necessary information upon a subject through the discussion of phenomena or of experimental facts, and he usually concludes with a statement that "such a phenomenon is known as diffusion," for example, or "this is called the latent heat". The matter chosen for discussion is well fitted for use with classes of students who are being encouraged to think independently, and is made interesting by the method of presentation. On the other hand, the depth to which each topic has been sounded will prevent even the most advanced of its students from feeling superiority to the treatment. It has evidently been prepared by one who has given the entire subject most careful attention and it should prove to be a very useful book.

W. R. WHITNEY.

**ESSAYS IN HISTORICAL CHEMISTRY.** BY T. E. THORPE. The Macmillan Co.: London and New York. xii + 582 pp. Price, \$4.00.

In this book are gathered sixteen addresses which have been



delivered by the author at intervals during the last twenty-eight years. Five of these have been added in the present edition. These are upon: Stanislao Cannizzaro; James Watts; Victor Meyer; On the Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century; and On the Development of Chemical Arts during the Reign of Queen Victoria. The style is very delightful and every chemist, and others as well, will find them very interesting and profitable reading. The individuals selected for discussion have been so well chosen that a perusal of the book will give the reader a very considerable insight into the development of chemistry during the last three hundred years.

The last essay of the list is, perhaps, the least satisfactory. While the work of English chemists during Victoria's reign was far from fulfilling the brilliant promise of the first quarter of the nineteenth century, it would certainly be possible to make a better showing for them than the author has here given. W. A. N.

**CHEMISCHES PRACTICUM.** I. Teil. Analytische Übungen, mit 25 Figuren im Text. BY DR. A. WOLFRUM. Leipsic. 1902. xvii + 562 pp. Price, 10 marks.

This book may be considered an attempt at a complete epitome of analytical chemistry, prepared especially for students who expect to devote themselves to chemical technology. It is divided almost equally into three parts, respectively: Qualitative Analysis, Quantitative Analysis, and Technical Analysis. One half of the first part and more than one third of each of the other two parts is given to organic analysis. The whole arrangement is systematic and in every way excellent. Most of the reactions involved, especially in the first part, are explained in accordance with the Ionic Theory.

Generally only one method of analysis is given, but with few exceptions the choice of methods is to be commended. In a few cases the book could have been brought a little closer to date. In the part devoted to technical analysis a brief description is given of the preparation of each metal and chemical product, so that this part of the book is also an epitome of chemical technology.

The fulness of the book is remarkable, for hardly an operation of analytical chemistry is omitted; for example, there are included the analysis of monazite sand, molecular weight determinations

by freezing- and boiling-point methods, toxicological analysis, gas analysis, oil analysis, preparation, analysis and testing of the coal-tar dyes.

When one takes into account the wealth of material compressed into a little more than 500 pages, it is obvious that the treatment cannot be critical nor the directions under each analysis sufficiently explicit to be of value to the student. It would be a good book from which to cram for an examination, and to the chemist it will be a useful book as an index, and outline of the principal processes of analytical chemistry and chemical technology. *Et praeterea nihil.*

JAS. LEWIS HOWE.

FIRST BOOK OF QUALITATIVE CHEMISTRY, FOR STUDIES OF WATER SOLUTION AND MASS ACTION. BY ALBERT B. PRESCOTT, PH.D., Director of the Chemical Laboratory, and EUGENE C. SULLIVAN, PH.D., Instructor in Analytical Chemistry, in the University of Michigan. New York: D. Van Nostrand Company. 1902. 148 pp. Price, \$1.50.

The plan of the authors of this, the eleventh edition of Professor Prescott's "First Book of Qualitative Chemistry," is given in the preface as follows:

"To enable the beginner in the qualitative laboratory to deal with chemical change in the light of the present studies of *water solution* and of mass action has been the main purpose in preparing this edition. With this intent the little book has been written anew throughout. It was first published by one of the authors in 1879, and designed then as now for classes taking a short course in qualitative practice."

The introduction gives 12 of its 24 pages to such topics as electrolytic dissociation, chemical equilibrium and hydrolysis. If some of these subjects could have been presented as simply as the other topics in the introduction, the book would have been less open to the criticism that the study of qualitative analysis is rendered unnecessarily difficult by presenting it from the standpoint of the dissociation theory. A number of strong arguments against this method of presentation may be given, but the question is not one that can be settled outside the laboratory. The burden of proof rests with the innovators and the present volume will be welcomed as another contribution toward the solution of the problem.

Aside from the debated question, the book has much to commend it. The matter is well arranged. The directions for the study of each analytical group, given under the heading "exercises with the ions," are admirable. They include such instructive experiments as the determination of the delicacy of the various separations and tests.

There are very few inaccuracies in the book. On page 51 in discussing the reduction of compounds of arsenic by means of potassium hydroxide and aluminum, it is stated that phosphoric acid interferes with this test for arsenic through the formation of phosphine.

THEODORE WHITTELSEY.

LOGARITHMISCHE RECHENTAFELN FÜR CHEMIKER. VON F. W. KÜSTER.

Dritte Auflage. Leipzig: Verlag von Veit and Co. 1902. Price, M. 2.00.

The success of this little book, as shown by the appearance of a second and third edition within a few years, is well deserved. It contains five-place logarithms and four-place mantissas; tables of atomic weights with multiples and logarithms; tables for the calculation of analyses; for the calculation of nitrogen and other gases; constants for molecular-weight determinations; a table for the determination of the volume of a flask from the weight of water or mercury which it contains at 18°; electrochemical constants; solubility of some substances at 15°; and tables for the preparation of normal solutions. The atomic weights used are the most recent, on the basis of O = 16. Unusual pains seems to have been taken to secure accuracy.

W. A. N.

THE ANALYSIS OF STEEL WORKS MATERIAL. BY HARRY BREARLEY AND FRED IBBOTSON. Longmans, Green & Co. 501 pp. Price, 14 shillings.

This book is divided into thirteen parts and an appendix. They comprise: I. The Analysis of Steel; II. The Analysis of Pig Iron; III. The Analysis of Steel-Making Alloys; IV. Rapid Analysis at the Furnace; V. The Analysis of Ores; VI. Analysis of Refractory Materials; VII. Analysis of Slags; VIII. Analysis of Fuel; IX. Boiler Water, Boiler Scales, etc.; X. Analysis of Engineering Alloys; XI. Micrographic Analysis of Steel; XII. Pyrometry; XIII. Miscellaneous Notes; Appendix, Bibliography of Steel Works Analysis.

The authors state in their preface that they "have dealt with

the analysis of steel works materials on such lines as could profitably be followed in a busy works laboratory," and that they "believe that the special standpoint from which the book has been written makes it no worse a text-book for technical schools and colleges." The processes given in the books that they have seen either, "(1) are too long and laborious, (2) require too delicate manipulation, (3) are too scanty in their treatment of the newer materials of steel-making, or (4) are not sufficiently accurate."

A series of methods which are not too long and laborious, do not require too delicate manipulation and yet are sufficiently accurate, would indeed be a boon to the profession and would deserve our gratitude and win our admiration. Careful study fails to show a single original method which answers this description or one which is in the smallest degree an improvement on those in use in our American steel works.

The descriptions of the methods for the analysis of steel are generally extremely sketchy and usually lack the details which would make them useful to the student.

For the determination of carbon the authors seem to favor direct combustion of the finely divided sample at a high temperature in a current of oxygen. They recommend sieving the sample to obtain the fine portion and claim that the fine and coarse portions contain the same percentage of carbon. This is contrary to the experience of many skilled analysts. A volumetric method which consists in oxidizing the carbonaceous residue with sulphuric acid and a weighed amount of bichromate, titrating the excess of chromic acid and calculating the carbon is certainly novel. Red lead is recommended as the best reagent for mixing with refractory alloys, such as ferrotungsten, ferrosilicon, etc., although they consider that bismuth trioxide would be preferable but for the price. No description is given of the Eggertz color method. For manganese the bismuthate process is evidently favored. It is an interesting process with points of decided merit.

Many methods are given for the determination of phosphorus but the one recommended by the authors consists in separating the phosphorus as phosphomolybdate, filtering, dissolving in ammonia, acidifying with hydrochloric acid, precipitating with lead acetate, filtering and weighing the lead molybdate, from the

weight of which the phosphorus is calculated. The authors do not refer to the use of the reductor with amalgamated zinc and give no details of the titration with caustic soda, the two methods most largely in use in this country.

The analysis of "Steel-making Alloys" is treated much more satisfactorily, and supplies a want which has existed ever since these alloys have come into general use.

The portion of the book treating of the "Micrographic Analysis of Steel" is clear and well written and is illustrated by well-chosen sections.

An appendix of 145 pages contains "A Bibliography of Steel Works Analysis" by Harry Brearley, which appeared in the *Chemical News*. The references are to English journals only. The other sections of the book call for no particular notice.

The text is occasionally marred by the use of such expressions as "weigh into", and of such words as "filtrable" and "combusted".

The book is clearly printed on excellent paper and is, among works on chemistry, the most creditable specimen of the book-makers' art that has been issued from the English press for some time.

It contains a full table of contents and an index.

A. A. BLAIR.

INTERNATIONAL CATALOGUE OF SCIENTIFIC LITERATURE. First annual issue. CHEMISTRY. Part I. London: Harrison and Sons, 45 St. Martin's Lane. Price, 21 shillings.

The Royal Society considered, about the year 1893, the advisability of printing a complete index of current scientific literature. It was hoped to do this by international cooperation; therefore, a large number of representative bodies and individuals abroad were consulted. After several meetings of accredited representatives it was concluded to proceed with the publication of such an index. Seventeen branches of science are included in this catalogue. Each complete annual issue will thus consist of seven volumes. The price of the set will be about \$90. Separate volumes will be sold. The first part of Volume D, devoted to chemistry, has just appeared. It will be followed shortly by a second part. This first volume consists of three sections: (1)

Schedules and indexes in English, French, German and Italian, (2) an author's catalogue, and (3) a subject catalogue. It is evident, from a careful examination of the present volume, that this international undertaking deserves the hearty support and cooperation of all scientific investigators, who will be kept fully and quickly informed of all new discoveries. The chemical volumes will be of real service to all chemists, and the entire catalogue should find a place in every library. S.

**QUALITATIVE ANALYSIS, A MANUAL FOR THE USE OF STUDENTS OF CHEMISTRY IN SCHOOLS AND COLLEGES.** BY L. M. DENNIS, Professor of Analytical and Inorganic Chemistry, and THEODORE WHITTELSKY, Instructor in Analytical Chemistry, Cornell University. Ginn and Co. 1902. pp. 142.

The aim of the authors is to offer "a work in qualitative analysis that shall be both exact and compendious, avoiding on the one hand the diffuseness of the larger treatises and on the other the incompleteness of the smaller manuals." Their method of instruction is to have the student observe the behavior of known substances in solution toward the following reagents: Potassium hydroxide, ammonium hydroxide, sodium carbonate, hydrogen sulphide, ammonium sulphide, hydrochloric acid, and sulphuric acid. This gives the basis for grouping, separation and identification. The analytical methods are generally well chosen and the directions clearly expressed. Following the latter, under the heading "Discussion," are given with suitable fulness the reasons for the various steps and also some consideration of the special difficulties which may be met in practice. The authors have been successful in maintaining a wise balance in the fulness of detail whereby the student receives sufficient information to work intelligently but is still called upon to exercise judgment and discrimination in the application of facts to special conditions. One might wish that the preliminary descriptions were made to include something more than reactions in solution. For example, some statement concerning oxides and their relation to acids, bases, and salts would seem desirable in order that the phenomena of oxidation and reduction might be better understood. It may perhaps be assumed that such information has been secured in a preceding course of general chemistry.

"The Introduction," in the words of the preface, "discusses in

considerable detail the principles and operations involved in qualitative analysis, but it does not include the consideration of the dissociation theory." For this, in the opinion of the writer, the authors are to be distinctly commended. Although the presentation of the ionization theory may accompany not unsuitably the subject of qualitative analysis, yet to base instruction upon it, to translate the statements of fact in so eminently practical a subject into the terms of a theory so hypothetical and still so controverted is, to say the least, not in the interest of sane teaching. The book is commended as one of the best of its class. A. V. E. YOUNG.

**THE ELEMENTS OF PHYSICS.** BY EDWARD L. NICHOLS AND WILLIAM S. FRANKLIN, in three volumes. New York: The Macmillan Company, reprinted 1901. Vol. I, **MECHANICS AND HEAT**, pp. 220; price, \$1.50 (electrotyped 1898.) Vol. II, **ELECTRICITY AND MAGNETISM**, pp. 272; price, \$1.90 (electrotyped 1896).

This work is not intended to include all the aspects of physical instruction. It contains only, as the preface indicates, "concise statements of physical laws, and a systematic development of principles." Without demonstrations of phenomena and an additional course of physical measurements, its excellence must be largely lost upon the student of physics. On the other hand within the compass of its contemplated field, and considering its real date, the work is unusually well balanced and adequate.

The mathematical method is sufficiently modern, and the lucid explanations of vector calculation and distributed quantity will be helpful to those not already familiar with these concepts. A knowledge of the calculus is of course presupposed. The treatment of physical dimension (in the technical sense) is important and not often so adequately emphasized. In view of this fact it is surprising to find occasionally such an equation as the following, (properly applied, of course, to unit volume):  $\text{Work} = \text{Pressure}$  (Vol. I, p. 117). This type of equation, by ignoring one dimension, seems to indicate the equality of two radically different dimensions. The data are less modern than the treatment. For example the weight of a cubic centimeter of hydrogen is recorded as 0.00008954 gram (Vol. I, p. 179). On page 8 the definition of *mass* does not seem to be convincing, and the importance of Newton's and Bessel's pendulum experiments in showing

the relation between mass and weight seems to have been overlooked.

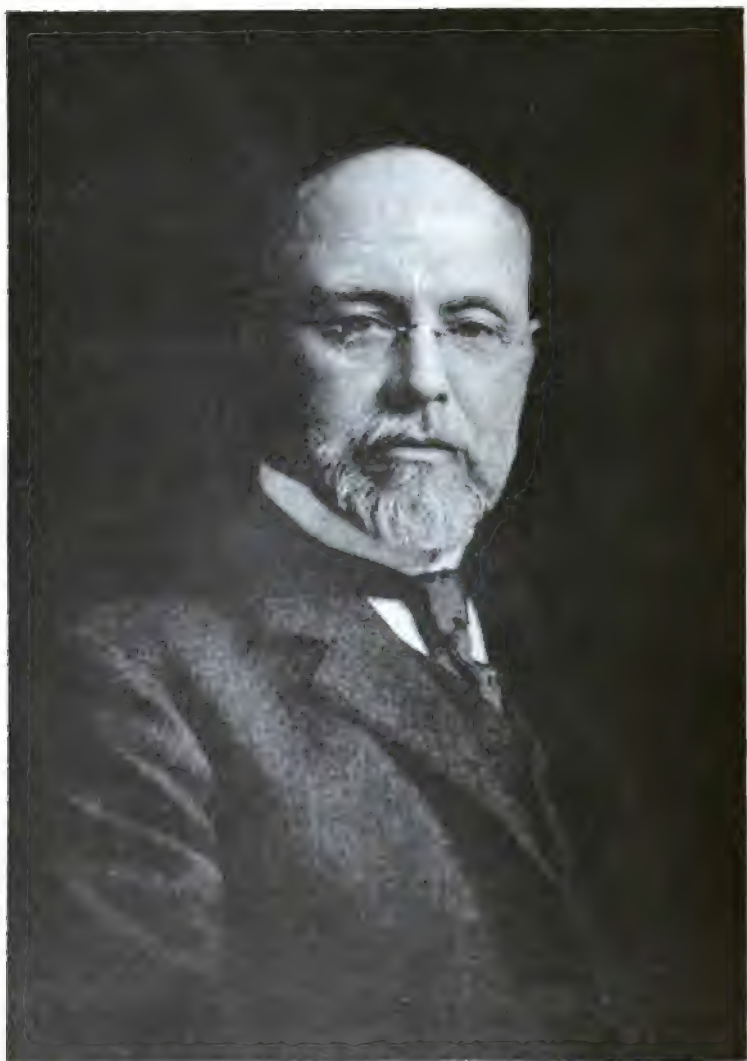
The second volume of the book is merely a reprint of the edition of 1896; hence, it does not contain descriptions of the Nernst lamp, the Rowland system of telegraphy, or the various practical systems of wireless electrical communication. It is much to be regretted that so good a book should not have been modernized in these respects in the new edition; unless indeed, the real date of the work were made obvious on the title page. Diplex, duplex and quadruplex telegraphy, the telephone, electric furnace, and ordinary electric lighting, are clearly treated. The modern electrochemist will find the treatment of the phenomena with which he is concerned quite inadequate, however.

In general, the work may be characterized as one very useful to him who, already possessing considerable physical knowledge, wishes a more thorough mathematical grasp of those generalizations which have stood the test of time.

THEODORE WILLIAM RICHARDS.







Yours sincerely  
Frank Benson.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### THE LIFE HISTORY OF A DOCTRINE.<sup>1</sup>

BY IRA REMSEN.

Received December 30, 1902.

THIS is the season of congratulation, and even if it were not, I should begin by congratulating my fellow members upon the present condition of our Society. We have every reason to be gratified. Statistics do not always convey a clear idea of the actual state of an organization, but they may be suggestive. The last annual meeting of the Society that was held in Washington occurred in 1897, just five years ago. At that time we had 1156 members. To-day the number has grown to 2176. The membership has nearly doubled. In 1897 the number of pages in the Journal of the Society for the first eleven months was 1315, while, for the corresponding period of this year, 2489 pages were published. To be sure, this included for 1902 the general index and the twenty-fifth anniversary volume. Omitting these, the figures are, for 1897, 1246, for 1902, 1956—an increase of 710 pages in five years. Any more rapid increase would almost be alarming.

One point suggests itself in this connection. Some of you may ask whether, under existing circumstances, it is desirable that there should be two journals in this country devoted to chemistry. Perhaps I am not the proper one to discuss this subject. There

<sup>1</sup> Presidential address delivered at the Washington meeting of the American Chemical Society, December 30, 1902.

seems to be an increasing demand for the American Chemical Journal as well as for the Journal of the Society. Having been in existence for nearly twenty-five years and being in robust health, the thought of giving up the ghost does not appear attractive to the former. It should, however, be clearly understood that there is no rivalry between the two journals, except such as may legitimately exist between friends, causing both perhaps to try to do their best. In these days of consolidation, the question may fairly be asked whether it would not perhaps be better to unite the two? It may be said that this subject has often been under friendly consideration, but the result has been unfavorable to consolidation. It must be confessed that the personal element enters into the discussion to some extent, and your speaker is the person involved. I feel more or less as though the American Chemical Journal were one of my children. Much of my activity has gone into the Journal for a quarter of a century. I have seen it develop from a feeble condition, through a dangerous second summer, through the usual list of children's diseases, until it was able to stand on its own feet and become self-supporting. While marriage is perhaps now in order, it is clear that this would involve a change of name and a loss of identity, and this I do not like to contemplate. So, my brethren of the Chemical Society, I ask you to bear with me for a few years longer. This independent journal will do our Society no harm. On the contrary, you may count on me to do all in my power to further the interests of the Society. One new reason why I do not want to give the journal up is that by force of circumstances I have, to some extent, recently been drawn away from my chemical bearings, and I do not wish as yet to occupy that position on the shelf that is, I suppose, awaiting me. My interest in chemistry is, I think, as great as it ever was, and I wish to do everything I can to keep up that interest. Through the journal I am necessarily kept more or less in touch with many of the active workers. While this is of no special importance to the workers, it is most helpful and refreshing to me, and, after a service of over thirty years in the ranks, I feel that I have a right to a pension. The only one I ask is the permission to continue as editor of my old journal without being subjected to the suspicion that I am an enemy of our Society and its constantly improving and now excellent Journal.

But this is all too personal, and I now pass to something impersonal. The general subject to which I ask your attention may be called "The Life History of a Doctrine". This title suggests a biological analogy. The life history of an animal includes a record of the events in the life of that animal from the earliest stages to the end—from birth to death. But there are events before birth. The life history is preceded by the embryonic history, and there are events after death—events biological, as shown in heredity; events chemical and physical as shown in decay and the reduction of the complex constituents of the animal to simple forms that can be assimilated by living things and thus enter again into the round of life. I do not refer here to spiritual events after death, for, in speaking of animals, I have not had man in mind, and it is customary, I believe, to deny to all animals, with this exception, the persistence of the spirit after death. In the analogy that I have in mind, however, the spiritual events are to be taken into account, for, as I think can be made clear, there is a life after death in the case of a good doctrine as in the case of a good man. The pursuit of this analogy is interesting (to me), but it will be more profitable to illustrate it by examples, of which there is no end. I wish especially to point out the bearing of the philosophy of the history of chemistry upon the present-day problems so far as this may be possible in the time at my disposal

The doctrine of the transmutation of metals played a most important part in its day. No one can trace it to its beginning. It is, however, clear, that it developed great strength and controlled the intellectual activities of the leading intellectual men of the world for several centuries. It led to the development of chemistry. The alchemists were the working chemists of their day. They taught the world the lesson that it is only by contact with the things of this world that we can gain knowledge of them. They laid the foundations of experimental science. The soul of alchemy was experiment. The fundamental doctrine of alchemy, transmutation, after a long and active life began to show signs of weakness; and in due time it took to its bed, and in spite of admirable medical care it died and was buried. No chemical doctrine has had anything like as long a life as this. To be sure, this could not have been possible, as the life history of the doctrine of transmutation covered a period longer than that which has elapsed since its death, though it is difficult to fix the time of its death

with accuracy. It is dead now at all events, and we may ask the question: What came after death? The doctrine accumulated large wealth and left the world a large estate. I need not give you the inventory. Probably no one can do so. But we do know that we owe to the activities of those who were controlled by the doctrine of transmutation a long list of substances that are of fundamental importance, such as sulphuric acid, nitric acid, phosphorus, alcohol, ether, etc. This is the material side of our inheritance. How about the spiritual? I have said that experiment was the soul of alchemy. That will live forever. I should perhaps have said that experiment was one of the souls of alchemy, for I suppose it is not objectionable to assume that a doctrine may have more than one soul. The rule in regard to human beings seems to be perfectly simple, and it is generally accepted, but I once heard of a professor, who, speaking of some great disaster, said: "On this occasion three hundred souls perished—counting one soul to each body." Assuming that a doctrine may have more than one soul, I am inclined to think that a second soul of alchemy is to be found in the idea of the relationship between the elements—an idea that persists and keeps dangling before us the possibility of the transmutation, not only of base metals into gold or silver, but of all the elements one into the other from one end of the list to the other.

Let us take another doctrine—that of phlogiston. The embryology of this doctrine has not been clearly worked out, but its life history has been traced pretty carefully. We know how it died and, in the events that followed, it is not difficult to find evidence of its existence after death. It was through the influence of this doctrine that chemists came to recognize the common features of those phenomena that we now group together under the general name of oxidation. They were all ascribed to one cause, a subtle substance, phlogiston. The search for this substance became the great problem of chemistry. The possibility of finding it was a great incentive to work. What matters it that the doctrine of phlogiston became aged and died and was buried? It did good service—ineestimable service. It kept its disciples at work and led them through this work nearer and nearer to the truth. In its life it passed through the period of infancy with all its attendant dangers, through the period of enthusiastic youth, through

sturdy manhood, and it reached old age with its attendant signs of weakness and decay. It died at last, but only after a mighty struggle. The act of dying was prolonged. Since then generations of astute teachers of chemistry have pointed out to their perhaps even more astute scholars the errors of phlogisticians, and they have all smiled and wondered how these deluded men could ever have been deluded. Possibly they forget that those at whom they smile were the leaders of their times, and that these leaders were trying as earnestly as the chemists of our own day to learn the truth.

What is the spiritual part of the doctrine of phlogiston that lives after its death? Clearly it is the idea that all the phenomena of combustion, including calcination, have a common cause. That cause has, to be sure, been shown to be oxygen. The phlogisticians thought that the cause was phlogiston, a purely imaginary substance. Priestley and Scheele and Lavoisier showed that it is an invisible gas working quite differently from the way the phlogisticians supposed. The life of the doctrine of phlogiston left us richer in material possessions and in ideas. The discovery of oxygen which is no doubt the most important discovery ever made in the field of chemistry, tended to give a materialistic trend to the thoughts of chemists. Both the philosopher's stone and phlogiston were imaginary substances that were sought in vain. Although both have been described by enthusiastic, but inaccurate, and perhaps mendacious, workers and writers, neither of these subtle things could be found. It was, nevertheless, possible to *believe* in their existence and to indulge in the hope of their discovery. But now oxygen came on the scene. Indeed, it may be truly said that it took possession of the stage, and it has been playing the leading part in the field of chemistry ever since. Here is an invisible substance existing in the air and capable of bringing about the most astonishing changes in things. We can not realize the effect of this discovery upon the thoughts of chemists. I sometimes feel that I should like to have lived as a chemist in the latter part of the eighteenth century. What thrills the workers of that time must have felt when they heard of the discovery of oxygen and learned from Lavoisier what part it played in combustion! We sometimes plume ourselves upon the doings of our own times. Has there ever been a more active or

more fruitful period in the history of chemistry than that wonderful period here referred to?

It was a great step forward to show that oxygen is one of the most powerful agents at work in the processes that are in progress on this earth. Not only combustion, but life in all its forms is in some way dependent upon it—animal life directly, plant life indirectly. Oxygen is the controlling factor in all the changes that are familiar to us. Some one, I do not know who, is responsible for that superficial and much quoted phrase "Without phosphorus no thought." The same statement could be made with equal truth in regard to other elements, such, for example, as nitrogen, carbon, hydrogen, sulphur, sodium, calcium, and, above all, oxygen. Indeed, we may almost say, without oxygen no chemical activity on this earth. This sudden appearance of oxygen and the recognition of its importance tended to put matter on a throne. "The study of material things will lead to the discovery of the hidden causes of other phenomena. See what the discovery of oxygen has done for us! Here is something tangible. Let us to work. There must be plenty of other things that operate as causes. If we can only bring these things to light, we shall be able to understand what is going on around us." So must the materialists have thought. There were, however, in those days, as there probably always have been, those who looked for the power behind the throne on which matter had been placed. To drop the figure and return to oxygen we may say that, while the discovery of this element gave the answers to many questions, it raised many new questions; and the attempts to answer these led again to regions of imagery.

One of the oldest tricks of the mind is the invoking of spirits in time of need. What causes all bodies to attract all others? We say gravitation, and somehow this spirit helps us. We feel as though we knew more about the phenomena of universal attraction when we have given a name to an imaginary and immaterial cause. So, too, when we inquire why oxygen causes the changes it is known to cause we can only conjure the spirits and give a new name. Oxygen unites with carbon; the carbon burns; a new thing is formed. It all becomes clear when we are told that it is chemical affinity that does it. Chemical affinity isn't an imaginary substance; it isn't something that we may see and handle. We haven't forgotten the philosopher's stone and



phlogiston. Our imaginary cause is spiritual; it is not material. But this is a digression. It was intended to show how the mind reverts promptly to the subtle, however powerful the attraction of matter may be. We cannot, if we would, keep to things material.

Recalling, what perhaps even I have forgotten, that my theme is "The Life History of a Doctrine," I propose, now that I have tried to show what is meant by this phrase, to move on more rapidly, so that I may dwell somewhat more fully upon one particular doctrine that has been before the chemical world in one form or another for about a century.

The discovery of oxygen did not lead directly to the introduction of a new chemical doctrine. Its chief result, as far as doctrine is concerned, was the death of the doctrine of phlogiston.

The discovery emphasized the importance of taking into consideration the weights of the things worked with. It was by this means that Lavoisier achieved his brilliant success. That weight was rather lightly regarded in earlier days may be seen from the following quotation, which is taken from an essay by Dr. Jean Rey, published in 1630:

"My chief care hitherto has been to impress on the minds of all the persuasion that air is heavy, inasmuch as from it I propose to derive the increase in weight of tin and lead when they are calcined. But before showing how that comes to pass, I must make this observation—that the weight of a thing may be examined in two ways, *viz.*, by the aid of reason, or with the balance. It is reason which has led me to discover weight in all the elements, and it is reason which now leads me to give a flat denial to that erroneous maxim which has been current since the birth of philosophy—that the elements mutually undergoing change, one into the other, lose or gain weight, according as in changing they become rarefied or condensed. With the arms of reason I boldly enter the lists to combat this error, and to sustain that weight is so closely united to the primary matter of the elements that they can never be deprived of it. The weight with which each portion of matter was endued at the cradle, will be carried by it to the grave. In whatever place, in whatever form, to whatever volume it may be reduced, the same weight always persists. But not presuming that my statements are on a parity with those of Pythagoras, so that it suffices to have advanced them, I support them with a demonstration which, as I conceive, all men of sense will

accept. Let there be taken a portion of earth which shall have in it the smallest possible weight, beyond which no weight can subsist: let this earth be converted into water by the means known and practiced by nature: it is evident that this water will have weight, since all water must have it, and this weight will either be greater than that of the earth, or less than it, or else equal to it. My opponents will not say that it is greater, for they profess the contrary, and I also am of their opinion: smaller it cannot be, since we took the smallest weight that can exist: there remains then only the case that the two are equal, which I undertook to prove. What is shown of this particle may be shown of two, three, or a very great number—in short, of all the element, which is composed of nothing else. The same proof may be extended to the conversion of water into air, of air into fire; and, conversely, of the last of these into the first."

The idea that a thing can be weighed by reason is, I suppose, an inheritance from the old philosophers who seem to have believed that all the problems of the universe could be solved by mental operations, or that any problem that could not be solved in that way was not worthy of their consideration. The first great generalization that was reached after the method of weighing was generally adopted by chemists was what we sometimes call the law of the indestructibility of matter, or, in more refined language, the law of the conservation of mass. Then followed the laws of definite and multiple proportions. Now a law of nature is quite a different thing from a doctrine. A law once discovered does not wither and die. It is eternal. Such a statement cannot be proved to be true. It calls for faith, but faith is called for at every turn in scientific matters as well as in spiritual. Without it progress would be impossible. As I am trying to deal with doctrines and not with laws, let me say that doctrines call for even a larger faith than laws. The very essence of a doctrine is faith in things unseen. The discovery of the laws of definite and multiple proportions led to the thought of atoms—not the evasive atoms of the Greeks, but atoms that could, in a way, be made the subject of experiment—the Daltonian atoms. This conception appeals to some minds very strongly. It is not necessary that we should know what the atoms look like, though this is highly desirable. The atom of chemistry can accomplish the purpose for which it was conceived by Dalton by simply standing for a unit of

matter that can pass unchanged, so far as mass is concerned, through a series of chemical changes. That is all we need to think of under ordinary circumstances. Some refined thinkers have found mental objections to the atom and it has been the subject of innumerable attacks. It doesn't do some things that it appears to us it ought to do and we try to depose it from time to time. Particles that cannot be more than 0.001 of the size of an atom challenge the right of the latter to supremacy, and the novelty-seekers, the born iconoclasts, cry out, "Make way for the corpuscle; the atom has had its day." But, seriously, the corpuscle does not seem to threaten the atom of to-day or of the immediate future—say any time within the next million years. The atom may be composed of corpuscles. Indeed, I think chemists would rejoice to learn that this is the fact. On this point, let me quote J. J. Thomson, the father of the new corpuscle. Speaking of Lenard's observation that the penetrating power of the corpuscles depends only on their density, he says: "This is exactly what would happen if the atoms of the chemical elements were aggregations of a large number of equal particles of equal mass, the mass of an atom being proportional to the number of these particles contained in it, and the atom being a collection of such particles through the interstices between which the corpuscle might find its way." "Since the density depends only on the number of particles in unit volume and is independent of the nature of the resulting atoms, Lenard's result is a strong confirmation of the view that the atoms of the elementary substances are made up of simpler parts all of which are alike." I am as yet unable to form a judgment in regard to the value of the evidence thus presented, but my confidence in J. J. Thomson gives me faith in the thoughts suggested by him. As I understand it, the worst that can be done for chemistry by the corpuscle is to change the atom so slowly that it would take something like a million years to enable us to detect the change by the balance. Perhaps the atomic weights of the elements, or of some of them, are undergoing change. Whether in the course of geological ages the atoms are becoming simpler or more complex is a question that appears idle at first, and yet when we bear in mind the fact that the atoms of our day have already been subjected to a great variety of influences for ages past, and that the atoms that we know are comparatively complex, we may at least suspect that the tendency so far is towards complexity. But here

we are face to face with a problem far beyond our powers—the action of eons upon ions.

Even if we assume the corpuscle, our conception is still materialistic, and we have to face the question, What is matter? That is a deep question—one of the deepest that can be asked. It is not difficult to show that all definitions of matter that have been given are totally inadequate; to show that matter is a product of the imagination; that we know matter only in so far as it affects our senses, and our senses are affected only by the different forms of energy. By logic we can easily, with Ostwald, reach the conclusion that "matter and energy are not to be thought of as distinct, as, for example, body and soul." We cannot help agreeing with him further when he says: "If we attempt to think of matter as separate from the various forms of energy nothing is left. Matter is, in fact, nothing but a group of different energies in space." But what is energy? This question would have been promptly referred to the physicists by the older chemists, but the chemists of to-day are physical chemists or chemical physicists, and they grapple with such questions without reserve. Perhaps the nearest approach to an answer is that of Herz, who, according to Ostwald, "expressly declines to see anything in the electromagnetic theory of light but a system of six differential equations." By means of mathematics, relations may be expressed and the story of nature told in a way that is clear to one who understands the language, and perhaps the time will come when men will have a complete record of the various forms of activity of nature, and they may then see that our mechanical and materialistic conceptions of natural phenomena are like the rude drawings of a child as compared with the paintings of Raphael. We have glimpses of such a scientific millenium in a few nooks and corners of physics. When that time shall come the physicists and chemists will in a way be superfluous. Everything will take the form of mathematics. By mental operations alone it will then be possible to solve such problems as may remain to be solved. It will then no longer be necessary to work with things—or rather with those manifestations of energy which in by-gone ages (say the twentieth century) had been crudely interpreted as indicating the existence of matter. A few models of molecules, of atoms, of corpuscles, and, I fear I must add, of ions, may then be preserved

in the archaeological institutes for the contemplation of mathematical philosophers.

What I have just said has not been intended as a criticism of any tendency. I have had that vision as others have. So, too, I have had visions of a heavenly kingdom to come, and I am thankful that this has been vouchsafed to me. But that heavenly kingdom is far away and so is that scientific millenium. Meanwhile there is work to be done here on earth and with earthly things. If we were all angels, a good many problems that now worry us would be solved—never to be solved again. So, too, in that scientific millenium such work as scientific men now do will not be called for. I sometimes think that the man with the distinctly mathematical mind must necessarily be unhappy if he applies himself to the study of natural phenomena. The points of contact between his language and the facts established are relatively so few that he must have sensations like those of a man with large wealth in a desert island. I once knew a young mathematician, even then distinguished, who had made something of a study of physics. He needed to add to his income and an opportunity offered itself to him to coach some students of physics. He tried this and had to give it up. One evening I found him in great distress. He told me that he had been trying to explain the law of falling bodies to his scholars and had failed to make any impression on them. He confessed that he himself had no conception of the significance of the law except as it appeared to him in a mathematical expression. He could not think of a falling body as such. The mathematical

expression  $\frac{dx}{dt} = gt + \text{constant}$ , however, made all clear. He tried to convey his own thoughts to his students and he was greeted with open-mouthed wonder. So, too, I knew a physicist who approached his problems in much the same way. He would not let his class of beginners work with a lever and deduce the law from the results of their own experiments, which to me appeared an instructive exercise, "for" he said "the lever is a mathematical instrument and it is not necessary to experiment with it in order to determine the laws of its action."

On the other hand, I have been told that Lord Kelvin says he cannot form a clear conception of any natural phenomenon without the aid of a model. I remember years ago, when he was

lecturing at the Johns Hopkins University, that he showed his hearers a beautiful model of light waves, and I am sure they had the power to convey light to a number of brains that would have been in darkness if any other method had been adopted. Whether we will or not, we have the non-mathematical mind to deal with, and this brings me back to chemistry and that special doctrine of chemistry that has to deal with atoms.

The doctrine of atoms is still alive though it came into being about a hundred years ago. It has been proved to be illogical as the ether that fills all space has been shown to be incapable of existence. Properties must be ascribed to the atom that it cannot possess and the same is true of the ether. What are we to do? Throw over the atom and the ether? Although both have been convicted of being illogical, I do not think it would be logical to give them up, for they are helpful in spite of their shortcomings, and in some way they suggest great truths. They are symbolic. It would be as illogical to give them up as it is, in my opinion, to deny the existence of a power in the universe infinitely greater than any of the manifestations familiar to us; infinitely greater than man; a power "that passeth all understanding." The atom helps us; the ether helps the physicist. We cannot give them up without losing our hold on many phenomena. For a century the phenomena of chemistry have been interpreted in terms of atoms. Take away that conception and, though it would be possible to deal with these phenomena, I cannot believe that they would appear as clear as they now do. In an address before the chemical section of the British Association for the Advancement of Science last summer Professor Edward Divers took as his theme "The Atomic Theory without Hypothesis." Let me quote a few passages from his address. He says: "The atomic theory of chemistry stands unsurpassed for the way in which it has fulfilled the purpose of every great theory, that of giving intellectual mastery of the phenomena of which it treats. But in the form in which it was enunciated, and still is universally expressed and accepted, it has the defect of resting upon a metaphysical basis, namely, upon the ancient hypothesis that bodies are not continuous in texture, but consist of discrete, ultra-minute particles whose properties, if known, would account for those of the bodies themselves. Hence it has happened that, despite the light it throws upon the relations of chemical phenomena and the simple means it affords of ex-

pressing those relations, this theory has always been regarded with misgiving, and failed to achieve that explicit recognition which its abounding merit calls for. Indeed, the desire has been expressed to see the time when something on a more solid foundation shall have taken its place." Professor Divers thinks that in dealing with chemical phenomena we can avoid thinking of discrete particles of matter. The law of constant proportions is, to be sure, entirely comprehensible as a law without the aid of the atomic theory, and so is the law of multiple proportions, but can we possibly, as yet, coordinate them without this aid? I do not think I can, and this doesn't worry me. The kind of atom that my mind's eye sees seems to help me, but that eye has not troubled itself with other attributes of the atom than that one which is needed. It will be remembered that in Dalton's time it was proposed to substitute for the atom the equivalent and some even wanted to use the conception of combining numbers. This last conception appeals to the systematic mind at first, but one cannot go very far with it without tacitly accepting the atomic theory. On this point Professor Divers says: "Refusing to commit themselves to belief in the hypothesis, chemists have thought from the first to escape the adoption of the atomic theory by putting Dalton's discovery into something like these words: Numbers, called proportional or combining numbers, can be assigned to the chemical elements—one to each—which will express all the ratios of the weights or masses in which substances interact and combine together. Perhaps," says Professor Divers, "the atomic theory is successfully set aside by expressing what is an actuality as an unaccounted-for possibility. But then those who use any such mode of expressing the facts without reference to the theory, never fail also to adopt the doctrine of equivalents, and thus, by this double act implicitly give in their adherence to the theory."

While the atomic theory can be used without using atoms, this must involve a great effort for the average mind. Why should we make the effort? If we can get a broader and deeper and clearer view of chemical phenomena by making the effort, by all means let us make it. Can we? That is the whole question. Apparently, not enough chemists have made the effort to furnish us with the necessary data upon which to base a conclusion. I should like to ask a dozen chemists to give me each his idea of the atom. The results would be interesting. Some years ago I sat

next the late Bishop Brooks at a dinner party, and I had an extremely interesting conversation with him. I remember many things he said and, as having some bearing on the question I am now dealing with, I quote this remark: "I am sure", he said, "that every individual has a different conception of God. If we could get at these conceptions we should probably be greatly surprised to find how markedly they differ from one another." Each individual injects his own personality into his conceptions, and the conceptions change according to circumstances.

At first, weight, or, more accurately, mass, was the only attribute of the atom that needed to be taken into consideration, except, of course, that power of combining with other atoms which is its fundamental attribute. Soon after the atom came to be a part of the chemist's equipment, two important attempts were made to add electrical charges to the atoms. Davy and Berzelius took different views of the way in which the electrical charges led to chemical acts, but they both agreed that chemical acts are essentially electrical. Every atom had, not only weight but an electric charge which did not add to its weight, but helped to explain its activity. The atom bore this charge for many years. It was thought that it gave it up and returned to its original simple form when the dualistic conception of the constitution of compounds gave way to the unitary conception. When it was found that chlorine, an electro-negative element, could take the place of the electro-positive hydrogen without creating any marked disturbance, chemists thought it best to turn their backs on the electro-chemical theory. In fact, the old electro-chemical theories in their original forms were untenable, but this is quite a different thing from saying that electrical charges have nothing to do with chemical action. It appears to-day that these electrical charges are the controlling factors in chemical phenomena, but of that farther on.

The next change that took place in the conception of the atom was that which followed the discovery of Frankland that there is a limit to the number of atoms that can combine with any other given atom. This was followed up by Kekulé and the doctrine of valence was the result. Atoms differ from one another in respect to the number of other atoms with which they can combine. It would be interesting to follow the life history of this doctrine of valence. It has had a most eventful career. It has been chastened



by experience, and now it appears to us freed, to a great extent, from the faults of youth. It is far from dead. Indeed it is probably at the beginning of its career. The phenomena of valence must be reckoned with and the study of these phenomena carries us back to the atoms and leads us to seek in them the causes of the differences in the composition of the compounds which are formed by their union.

It has unquestionably been shown that the original form of the doctrine of valence is not tenable. Elements cannot be classified rigidly under a few heads as univalent, bivalent, trivalent, quadrivalent, etc., nor can we hold the other view that all the elements have either an even number or an odd number of valences or bonds, though there appears to be some truth in this latter view. The artiads and perissads of our youth may return to us, but before they are received it will be necessary for us to ask them a few questions, and for them to answer them satisfactorily. In fact, we have learned that the phenomena of valence need to be studied carefully before we can discover the laws that govern them. The views that prevail to-day are but the foreshadowing of a broader conception of valence. This subject is very much to the front at present. The speculations of Werner with reference to complex inorganic compounds have awakened wide interest and have set many to thinking. One cannot ignore the mass of evidence put forward by Werner that tends to show that in many compounds it is necessary to assume the existence of a core or inner sphere consisting of a group of atoms in combination, this core holding in combination a definite number of atoms or groups. Whether that which holds together the atoms that make up the core is what in simpler compounds manifests itself as valence remains to be seen. At all events, if the views of Werner should prove to be correct, we shall have two kinds of valence to deal with—that of the inner sphere and that of the outer sphere, or that of the core and that of the shell. In a recent article Werner extends his views and introduces the conception of secondary valences. Thus he holds that in ammonia the three valences that enable the nitrogen atom to hold the three hydrogen atoms in the molecule of ammonia are different from that which enables ammonia to combine with a molecule of hydrochloric acid. The former he calls the "primary valences" (*Hauptvalenzen*), the latter a "secondary valence" (*Nebenvalenz*). He does not think

that the two differ fundamentally. So Thiele in his study of the phenomena of saturation among organic compounds is obliged to assume the existence of "partial valences (Partialvalenzen), and the facts described by him are singularly in accord with the assumption. This applies up to the present only to the compounds of carbon. Thiele's "partial valences" are, however, not to be confounded with the secondary valences of Werner or the other earlier "residual valences" of Armstrong. A discussion of this subject might be made interesting and profitable, but I cannot go into it here. So many curious valence phenomena have been observed of late that one cannot help feeling that we are about to have a revelation that will make the old as well as the new phenomena appear clear. Carbon is bivalent and quadrivalent. That has always been clear, though Nef has made it clearer than it used to be. But now comes trivalent carbon that Gomberg has shown us, and we may be prepared for almost anything. And oxygen that has been regarded as a very model of bivalency these many years is getting restless, and is beginning to show that it too can do the unexpected. It seems clear that it can act as a quadrivalent element, but, according to Walden, it has even higher powers.

Whatever may come of all this, it is clear that we must enlarge our conception of the atom. It not only has the power to combine with other atoms, but under given conditions it has a definite number of such powers. If we attempt to represent these powers to our minds we can only use the grossest methods. The union of two univalent atoms does not necessitate the conception of direction. But when two univalent atoms unite with one bivalent atom we can hardly avoid thinking of two points of contact on the bivalent atom and of two directions in which it exerts its powers of combination. This conception of direction is, further, forced upon us by a study of the phenomena of stereochemistry, especially in the field of the chemistry of the compounds of carbon. But, if the carbon atom exerts its powers of combination in definite directions that can be determined by observation, it is, to say the least, highly probable that all other elements act in the same general way, and indeed many facts have been discovered within the last few years that have given a clue to the stereochemistry of nitrogen, of sulphur, of silicon and other elements. Indeed, in the studies of Werner, already referred to, stereo-

chemical phenomena are illustrated in many ways by compounds of platinum, palladium and other metals that enter into the complex inorganic bases.

Our imaginary atom then has mass. It has the power to combine with other atoms under the proper conditions. This power is either a unit as in the univalent elements, or it is divisible by 2, 3, 4, 5, 6, 7 or 8 in the case of other elements. Further, one and the same element may exhibit different powers under different conditions, but the laws governing these variations are not known. Finally, the powers of combination of a polyvalent atom are exerted in definite directions that can to some extent be determined. These directions are evidently subject to variation, and some effect upon a compound caused by displacement has apparently been shown in the case of some carbon compounds; at least Von Baeyer's strain theory is based upon this assumption.

The latest turn that has been given to the conception of the atom brings in again the electric charge. It appears that the contemporaries of Berzelius were too easily frightened, and Berzelius was nearer right than they supposed. Every book on the history of chemistry has an obituary on the electrochemical theory of Berzelius. But now it appears that the electrical charges assumed by him must be assumed by us. These have come more and more to the front of late, and chemical union is being regarded more and more as due to the interaction of these charges. According to the modern conception, an atom may or may not be carrying a charge of electricity. When carrying its charge it is called an ion, and it is then ready for action. When the elementary ion gives up its charge, either by entering into combination with another ion, or other ions, or by being set free, it becomes an atom. But more than this. The electrical charge of an ion is either a unit charge or a multiple of this. The bivalent ion has two charges, the trivalent ion has three, etc. The experimental basis for these ideas is found in the electrolytic phenomena that are included in the scope of Faraday's law. Faraday found that a definite quantity of electricity causes a definite amount of decomposition in a conductor of the second class; and, further, he found that when the same current is passed through solutions of the salts of different metals in series, the masses of the different metals that separate are proportional to the combining weights or the equivalents of these metals. To make clear the full signifi-

cance of these facts would require more time than is at my disposal. Suffice it to say, that in terms of our present theory it takes twice as much electricity to set a bivalent atom free as to set a univalent atom free; three times as much for a trivalent atom, etc. How to conceive of one, two, three, or four charges of electricity on an ion I leave to the physicists to explain, though it must be said that they are not in the least called upon to explain.

The atom has thus been followed in its career down to to-day. The changes in our conceptions have been traced sufficiently for our purpose. It is at present a bundle of attributes and with these attributes it is a convenient nucleus for thought. Nothing has been said of the dynamics of the atom, by which I do not, of course, mean chemical dynamics in general. So far as the atom is concerned our knowledge of its motions may perhaps fairly be summed up by saying that it seems probable that it moves in some mysterious way, and perhaps the phenomena of chemistry are all due to this motion. But that carries us into the region of speculation pure and simple, and in this region the scientific worker feels uncomfortable. The atmosphere is too rarefied for him.

If you now ask what is the soul of the doctrine of atoms? I can only answer that this soul is still in the course of development. The doctrine has some immortal attributes, but what will live after its death is too early for any one to say.

*"Prove all things. Hold fast that which is good."*

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 74.]

### ON THE COMPOSITION OF COWS' MILK.

BY H. C. SHERMAN.

Received October 10, 1902.

In general the percentage of fat in cows' milk varies much more than that of the other constituents. It is probably safe to say that a variation of 3 per cent. in fat is as common as a variation of 1 per cent. in the total amount of other solids. Milk is apt to be regarded, therefore, as consisting of a serum of quite uniform composition in which is suspended a variable amount of fat. It is, however, a matter of some importance both from the physiological standpoint and as an aid in judging suspected

samples, to define as accurately as possible the normal variations of each of the chief constituents and to determine whether any change in the amount or relative proportion of proteids, sugar or ash is connected with the fluctuations in the fat content.

With the aid of friends connected with a large dairy farm, the writer has been able to obtain a considerable number of samples, the analyses of which seem of sufficient interest to warrant publication. These samples fall mainly into two groups: (1) periodical samples of the mixed milk of a large herd, intended to show the normal variations of composition during the year, and (2) samples above or below the average in fat or in solids-not-fat, analyzed to ascertain whether any other constituent varies with the fat, and to which constituent the variations in the solids-not-fat is chiefly due.

*Methods of Analysis.*—The analytical methods used were those of the Association of Official Agricultural Chemists<sup>1</sup> and the details of manipulation were uniform throughout. Fat was determined by the paper coil method, the milk being very thoroughly dried on the coil and then extracted with anhydrous ether. The percentages of protein<sup>2</sup> were obtained by multiplying the percentages of nitrogen found by the Kjeldahl method by 6.25, the digestion with sulphuric acid being continued for about two hours after the liquid had become colorless. Ash was determined by direct ignition at the lowest possible dull red heat. Milk-sugar was determined by difference, the sum of the percentages of fat, protein and ash being subtracted from the percentage of total solids found by drying to constant weight in a flat-bottomed dish at the temperature of boiling water. The samples were preserved by the addition of formaldehyde in the proportion of 1 drop of the commercial 40 per cent. solution to each ounce of sample. In the experience of this laboratory the use of such an amount of formaldehyde has not been found to have any appreciable effect upon the analytical results.

*Source of Samples.*—All of the samples analyzed were from one large farm in Westchester County, New York. The herd contained about 600 milk cows of which about 200 were pure bred Jerseys and the rest mainly "Jersev

<sup>1</sup> Bulletin 46, revised edition, Bureau of Chemistry, U. S. Department of Agriculture.

<sup>2</sup> In accordance with the terminology adopted by the American Association of Agricultural Colleges and Experiment Stations, the term "protein" is used to designate the value (nitrogen  $\times$  6.25).

grades." From 450 to 500 cows were usually milked at a time, the others either being dry or allowed to run with their young calves. Though divided into several groups, the entire herd was under one herdsman, who stated that throughout the year each cow received hay or green fodder and one and one-half pounds of oil meal per day, and in addition to this was fed with a mixture of one-half wheat bran, one-quarter crushed oats and one-quarter corn meal. The amount of this mixture fed depended upon the judgment of the feeder and to some extent upon the season and the demand for milk, but was always liberal. Exercise was allowed freely except in very severe weather and in summer there was pasturage, though this was never depended upon to the exclusion of other food. The cattle were always comfortably housed and were milked at 4-30 to 5.00 A.M., and 3.30 to 4.00 P.M.

*Morning and Afternoon Milk.*—Frequent tests of the mixed milk of the herd showed that the afternoon milk contained quite regularly about 0.4 per cent. more fat and practically the same solids-not-fat as the milk yielded in the morning. Similar results have constantly been found by Richmond<sup>1</sup> in the great numbers of analyses made yearly in his laboratory. Moreover, it has been found at the New York State Experiment Station<sup>2</sup> and by Fruhling and Schultze,<sup>3</sup> in each case as the result of many analyses, that neither protein, sugar nor ash shows any distinct tendency to be higher at one milking than at the other, or, in other words, that the difference in composition between morning and evening milk is a difference in fat content only and does not extend to the other constituents. Linfield<sup>4</sup> has recently reached the same conclusion which is confirmed for the herd here studied in the following experiment by the writer.

On April 19, 1901, the milk obtained at each milking was carefully sampled and analyzed, with the following results:

	Fat.	Protein.	Sugar.	Ash.
Morning milk .....	4.85	3.68	4.85	0.74
Afternoon milk .....	5.22	3.65	4.90	0.73

Further experiments on this point were therefore considered

<sup>1</sup> "Dairy Chemistry," p. 126 and papers in *The Analyst*.

<sup>2</sup> Report for 1891; Abstracted in Experiment Station Record, 4, 257.

<sup>3</sup> Quoted by Stohmann: "Milch und Molkereiprodukte," p. 166.

<sup>4</sup> Utah Experiment Station Bulletin 68, p. 234.

unnecessary and in studying the variations of composition from month to month only the afternoon milk was sampled.

#### SEASONAL VARIATIONS IN COMPOSITION.

It is well known that milk tends to be richer, both in fat and in solids-not-fat, in winter than in summer, and Richmond's analyses have shown that the milk received from English farms varies in practically the same way each year, the difference between the highest and lowest monthly averages being about the same for fat as for solids-not-fat and amounting usually to 0.3 or 0.4 per cent.

For two years, beginning with April, 1900, the mixed milk of the herd above described was sampled and analyzed once each month. As the milk came to the dairy in cans of uniform size, an accurate sample was readily obtained by means of the Scovell sampling tube. The composition of these samples is shown in Table I, below.

TABLE I.—COMPOSITION OF MONTHLY SAMPLES.

Month.	Total solids.	Fat.	Solids-not-fat.	Protein.	Sugar.	Ash.
January, 1901... ..	14.69	5.36	9.33	3.76	4.83	0.74
“ 1902.....	14.82	5.35	9.47	3.82	4.89	0.76
“ average ....	14.76	5.36	9.40	3.79	4.86	0.75
February, 1901 .....	14.53	5.24	9.29	3.67	4.87	0.75
“ 1902 .....	14.73	5.38	9.35	3.72	4.88	0.75
“ average ...	14.63	5.31	9.32	3.70	4.87	0.75
March, 1901 .....	14.39	5.19	9.20	3.57	4.90	0.73
“ 1902 .....	14.52	5.37	9.15	3.57	4.84	0.74
“ average.....	14.46	5.28	9.18	3.57	4.87	0.74
April, 1900 .....	14.25	5.14	9.11	3.48	4.88	0.75
“ 1901 .....	14.43	5.13	9.30	3.66	4.89	0.75
“ average .....	14.34	5.14	9.20	3.57	4.88	0.75
May, 1900 .....	14.37	5.22	9.15	3.58	4.84	0.73
“ 1901 .....	14.25	5.12	9.13	3.54	4.84	0.75
“ average.....	14.31	5.17	9.14	3.56	4.84	0.74
June, 1900.....	14.26	5.10	9.16	3.59	4.85	0.72
“ 1901.....	14.64	5.38	9.26	3.59	4.91	0.76
“ average .....	14.45	5.24	9.21	3.59	4.88	0.74
July, 1900 .....	14.13	5.00	9.13	3.54	4.84	0.75
“ 1901 .....	14.23	5.29	8.94	3.50	4.71	0.73
“ average .....	14.18	5.15	9.03	3.52	4.77	0.74
August, 1900 .....	14.11	5.00	9.11	3.58	4.79	0.74
“ 1901 .....	14.34	5.28	9.06	3.54	4.78	0.74
“ average .....	14.23	5.14	9.09	3.56	4.79	0.74
September, 1900 .....	14.73	5.39	9.34	3.75	4.84	0.75
“ 1901 .....	14.34	5.27	9.07	3.56	4.77	0.74
“ average ..	14.54	5.33	9.21	3.66	4.81	0.74

Month.	Total solids.	Fat.	Solids-not-fat.	Protein.	Sugar.	Ash.
October, 1900.....	14.46	5.23	9.23	3.73	4.75	0.75
“ 1901.....	14.98	5.48	9.50	3.87	4.89	0.74
“ average ....	14.72	5.36	9.36	3.80	4.82	0.74
November, 1900 .....	14.78	5.35	9.43	3.82	4.86	0.75
“ 1901 .....	14.81	5.32	9.49	3.87	4.86	0.76
“ average ..	14.80	5.34	9.46	3.84	4.86	0.76
December, 1900 . . .	14.52	5.20	9.32	3.77	4.79	0.76
“ 1901 .....	14.77	5.34	9.43	3.85	4.81	0.77
“ average ..	14.65	5.27	9.38	3.81	4.80	0.77
General average. ....	14.71	5.26	9.25	3.66	4.84	0.75

During the time covered by these analyses there was no change in the system of feeding or management and samples were not taken during or immediately after very sudden changes in the weather. The large size of the herd and its divisions into separate groups would minimize any variations which might be due to individual peculiarities or accidental causes, and as there were few changes in the herd and the number of fresh cows did not fluctuate very greatly from month to month, it seems safe to conclude that the differences shown by the monthly averages are due to influences very closely connected with the season and that they may be called seasonal variations.

The diagram on the opposite page is designed to show the variations here found, together with those previously reported by Richmond<sup>1</sup> and by Van Slyke.<sup>2</sup>

In the diagram the results above given are represented by solid, those of Richmond by broken, and those of Van Slyke by dotted lines. Richmond determined only fat and solids-not-fat. Van Slyke's analyses, while including the determination of protein, were made primarily for another purpose and cover only a part of the year.

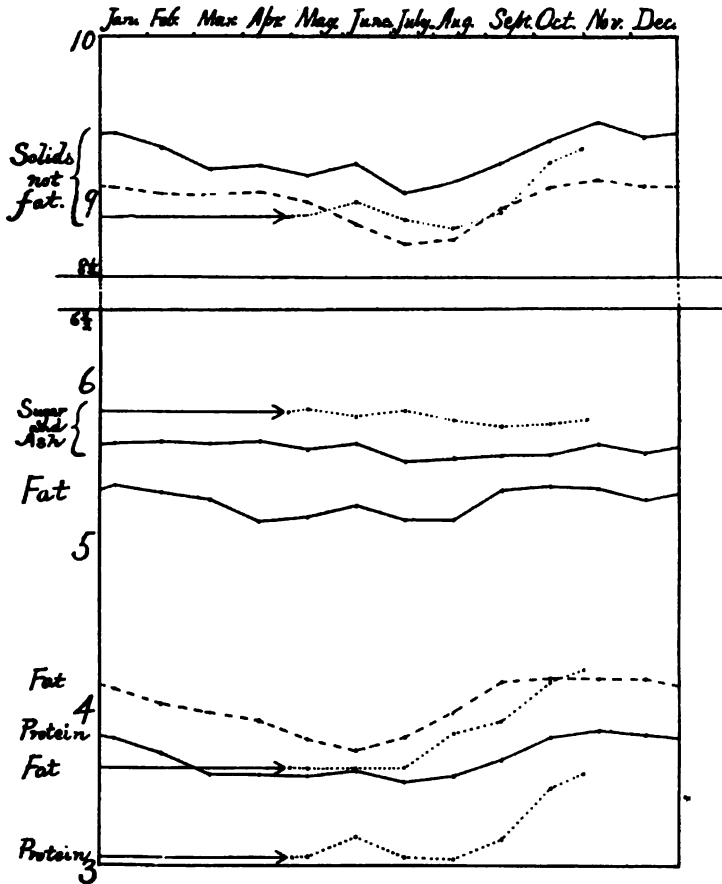
Richmond's results for fat and for solids-not-fat run nearly parallel. As regards solids-not-fat the writer's results are practically parallel with those of Richmond. On fat, our results are similar to those of Richmond but show less decrease in mid-summer. This is probably due to the fact that the herd here studied was managed with special reference to the production of milk of uniformly high fat content. The milk of this herd was

<sup>1</sup> "Dairy Chemistry," p. 128 (afternoon milk for 1896). Richmond's more recent analyses show monthly variations of the same character.

<sup>2</sup> Averages of data obtained by analysis of milk delivered to certain cheese factories during the summers of 1892-'94, summarized in the report of the New York State Experiment Station for 1894.



richer during the second summer than during the first. The results for the first twelve months would be found nearly parallel to Richmond's.



Van Slyke's results show a greater rise in both fat and solids-not-fat in the autumn, but this is explained by the fact that most of the cows in the herds observed by him had calved in the spring, so that in passing from summer to autumn we find the combined effects of season and of advancing lactation.

Considering the circumstances just mentioned, the three sets of curves show a very close agreement and in each case there is a very evident tendency for the fat and solids-not-fat to rise and fall nearly together.

Passing to the other curves we find the sugar-and-ash percentages<sup>1</sup> to be nearly uniform, the extreme variation between monthly averages being only about 0.1 per cent., while the protein runs parallel with the solids-not-fat. In other words, the seasonal variations in solids-not-fat are practically variations in protein, the percentage of sugar and ash remaining nearly uniform throughout the year.

#### COMPOSITION OF SPECIAL SAMPLES.

During the time covered by the monthly analyses recorded above several samples of milk from individual cows or from certain groups of cows in the herd were analyzed. For convenience, most of the samples from individual cows can be grouped in two classes.

*Some Unusually Rich Samples.*—These samples were taken at random from among many of similar richness. Table II shows the composition of these samples and, where ascertained, the daily yield of milk, and the number of months since the last calf.

TABLE II.—COMPOSITION OF SOME UNUSUALLY RICH SAMPLES.

No.	Months since last calf.	Milk per day. Pounds.	Total solids. Per cent.	Fat. Per cent.	Solids-not-fat. Per cent.	Protein (N × 6.25). Per cent.	Milk-sugar. Per cent.	Ash. Per cent.
1	..	..	19.88	8.96	10.92	5.11	4.95	0.86
2	10	9½	19.21	8.94	10.27	4.92	4.55	0.80
3	10	4½	18.99	8.83	10.16	4.38	4.97	0.81
4	"nearly dry"		18.74	8.14	10.60	4.81	4.94	0.85
5	7	9	18.44	7.84	10.60	4.91	4.91	0.78
6	..	12	18.24	7.72	10.52	4.87	4.87	0.78
7	2½	21	17.81	8.04	9.77	3.97	4.96	0.84
8	12	6	17.70	7.42	10.28	4.80	4.66	0.82
9	9	11½	17.70	7.07	10.63	4.96	4.84	0.83
10	10	..	17.28	7.05	10.23	4.80	4.61	0.82
11	..	10	16.83	6.98	9.85	4.59	4.45	0.81
12	3½	14	16.81	6.61	10.20	4.51	4.81	0.85
13	9	8½	16.73	7.34	9.39	4.23	4.31	0.85
Average .....			18.03	7.76	10.27	4.68	4.76	0.83

It will be noticed that richness in fat is accompanied in each of these cases by richness in solids-not-fat, while four of the thirteen samples equal or exceed in solids-not-fat the figure given by Richmond<sup>2</sup> as the highest which had come under his notice. This

<sup>1</sup> The writer's results for sugar and ash are here combined in order to facilitate comparison with those of Van Slyke. A small variation in ash following that in protein will be noted later.

<sup>2</sup> "Dairy Chemistry," 1899, p. 120.

increase in solids-not-fat occurs almost entirely in the proteids, which average about 1 per cent. higher in this group of samples than in the mixed milk of the entire herd. In most cases the cows were well advanced in lactation and the yield of milk was rather small. Seven of the samples were from pure-bred Jersey cows and six from Jersey-grades.

*Samples Low in Solids-not-fat.*—The six samples shown in Table III were all from healthy cows. The first five were obtained during the hot weather of August, 1901. The sixth was from the same cow as the fifth, but was taken three months later. This is the only case in any of the tables where two samples from the same cow are given. While these samples vary considerably in fat content, they are alike in containing low percentages of solids-not-fat.

TABLE III.—SAMPLES LOW IN SOLIDS-NOT-FAT.

No.	Mon hs since last calf.	Milk per day. Pounds.	Total solids. Per cent.	Fat. Per cent.	Solids not-fat Per cent.	Protein (N × 6.25). Per cent.	Milk- sugar. Per cent.	Ash. Per cent.
1	6	10½	14.29	6.09	8.20	3.66	3.78	0.76
2	9½	11	11.97	3.71	8.26	3.55	4.00	0.71
3	2	26½	10.83	2.64	8.19	2.86	4.58	0.75
4	9	7	10.65	3.27	7.38	3.24	3.43	0.71
5	7	8	11.77	4.69	7.08	3.57	2.81	0.70
6	10	6½	9.66	2.97	6.69	3.17	2.86	0.66
Average .....			11.53	3.90	7.63	3.34	3.59	0.71

The percentages of proteids are here somewhat lower than in Table I, but are not low in proportion to the fat present. Averaging the six analyses it happens that the fat percentage is practically that which has been found as the general average for ordinary cows' milk. It is noticeable that the averages for protein and ash are also strikingly close to the estimated general averages, while the sugar is here considerably below the normal average. In other words, the deficiency of solids-not-fat is all in the milk-sugar. This is in accordance with Richmond's opinion<sup>1</sup> that "when genuine samples are low in solids-not-fat, the proteids and ash are normal and the milk-sugar is the constituent on which the deficiency falls."

#### RELATIONS BETWEEN THE PRINCIPAL CONSTITUENTS.

*Relation of Protein to Fat.*—Timpe<sup>2</sup> announced in 1899, appar-

<sup>1</sup> *The Analyst*, 28, 226.

<sup>2</sup> *Chem. Ztg.*, 23, 1040.

ently on the basis of less than thirty analyses, that there exists a definite quantitative relation between the percentages of fat and proteids in cows' milk which may be expressed by the formula  $\text{proteids} = 2 + 0.35 \text{ fat}$ . A similar conclusion, though differently expressed, had been reached by Cooke<sup>1</sup> some years earlier as the result of an extensive compilation of American analyses. Cooke found that in milks containing not less than 13 per cent. of total solids, the milk-sugar is nearly constant while "the proteids increase with the total solids, being always about one-fourth." Since the other three-fourths of the increase is practically all fat it is evident that this relation might be expressed by a formula almost identical with that of Timpe. The work of the latter was, however, strongly criticized by Richmond,<sup>2</sup> who gives the average results of analyses of about fifty samples grouped according to fat content and concludes that while there is a tendency for the proteids to be higher when the fat is high, this tendency is very much less than that indicated by Timpe's formula. Comparing the average results found by Woll<sup>3</sup> in testing cows of different breeds, it appears that he failed to find the differences in protein quite as large in proportion to the differences in fat as the formula would indicate.

Applying to the analyses given above the formula which expresses the conclusion reached by Cooke ( $\text{protein} = 2 + \frac{1}{3} \text{ fat}$ ) we find that with samples from individual cows there may be considerable discrepancies, but if we take the average milk of the herd for the year or the average of Table II or of Table III, the figure for protein given by the formula is within 0.1 per cent. of the amount actually found. To test this point further the following samples were analyzed: (1) a composite sample of the milk of 14 cows taken at random from among those low in fat, (2) the mixed milk from a group of about 100 cows which had been regularly found below the average of the herd in fat content, (3) the mixed milk from a group of about 100 cows of which a large proportion were well advanced in lactation, and (4) a sample of the mixed milk of the entire herd taken in May, 1902, when fresh pasture and a change in the grain ration had produced a temporary rise in fat content. The analyses of these samples follow:

<sup>1</sup> Vermont Experiment Station Report for 1890, p. 97.

<sup>2</sup> *The Analyst*, 28, 225.

<sup>3</sup> Wisconsin Experiment Station Report for 1901, p. 85.

No.	Total solids. Per cent.	Fat. Per cent.	Protein. Per cent.	Milk-sugar. Per cent.	Ash. Per cent.
1	12.78	3.91	3.25	4.92	0.69
2	14.34	5.07	3.64	4.89	0.74
3	15.39	5.67	4.03	4.87	0.82
4	15.05	5.76	3.77	4.75	0.77

In each of the first two samples the percentage of protein is within 0.05 per cent. of that which would be calculated from the formula. In (3), where the richness of the milk was due chiefly to advanced lactation, the increase in protein is more than one-third of the increase in fat, while in (4), where the fat content was temporarily increased by a change of food, the increase in protein is less than one-third as great.

The data at present available indicate that aside from the seasonal variation already noticed, the percentages of fat and protein tend to rise and fall together, though not to the same extent, that the average relation between the two is approximately expressed by the formula, protein =  $2 + \frac{1}{3}$  fat, but that the protein often shows less variation from the average than this formula would imply.

*Relation of Ash to Protein.*—According to Richmond<sup>1</sup> the percentage of ash may be deduced with fair accuracy from that of protein by the formula, ash =  $0.36 + 0.11$  protein. Most of the analyses given in this paper had been made and the tendency of the ash to vary with the protein had been noticed when the above formula was published. On applying it to our results, we find a very close agreement between the percentages of ash calculated and those actually found. The discrepancies were as follows: (1) In 24 samples of the mixed milk of the herd, from + 0.05 to - 0.01, average + 0.015 per cent; (2) In 7 samples of mixed milk from groups of 6 to 100 cows, from + 0.05 to - 0.02, average + 0.021; (3) In 23 samples of milk from individual cows, four of which contained over 5 per cent. of protein, from + 0.12 to - 0.08, average + 0.033. If the formula be modified to read ash =  $0.38 + \frac{1}{10}$  protein, an even better agreement is obtained, the above discrepancies becoming, respectively, (1) from + 0.03 to - 0.02, average + 0.001; (2) from + 0.02 to - 0.04, average 0.000; (3) from + 0.09 to - 0.08, average + 0.010.

*Relation of Milk-Sugar to Other Constituents.*—The analyses do not indicate that the milk-sugar has any tendency to rise and

<sup>1</sup> *The Analyst*, 26, 310.

fall with any other constituent. In normal milk the percentage of sugar in the serum seems to be very nearly constant. Certainly it shows smaller relative variations than any other of the principal constituents and such variations as occur are usually so irregular as to appear accidental. Analytical errors also would be larger here than elsewhere, inasmuch as the milk-sugar is usually estimated by difference. In milk showing an unusually low percentage of solids-not-fat, the deficiency is found to be principally in the milk-sugar. Such milk may be yielded by healthy cows and is most commonly but not exclusively found in hot, dry weather. Occasionally there may be in midsummer a sufficient number of such cases to cause an appreciable lowering in the sugar content of the mixed milk of a large herd, but ordinarily there seems to be no seasonal variation in the percentage of milk-sugar such as is found in the case of fat, of protein, and to some extent also of ash.

#### SUMMARY.

As all of the samples analyzed were from one herd of cattle, the following statements, while summarizing the results which we have obtained, may not be equally applicable to milk produced under other conditions.

Monthly analyses extending over two years showed the percentage of protein, like that of fat, to vary with the season, being higher in fall and winter than in spring and summer, while the percentage of milk-sugar remained nearly constant throughout the year.

In general, a milk rich in fat will also be rich in protein. In these analyses the excess of protein above the normal averaged about one-third as much as the excess of fat.

All of the results obtained accord with the conclusion recently reached by Richmond that any deficiency of solids-not-fat is chiefly due to a deficiency in the milk-sugar, while any excess above 9 per cent. is chiefly due to an excess of protein.

In practically all of the samples examined the relation between protein and ash was very nearly that found by Richmond and expressed by the formula,  $\text{ash} = 0.36 + 0.11 \text{ protein}$ . To agree more exactly with our averages, the formula may be modified to read  $\text{ash} = 0.38 + \frac{1}{10} \text{ protein}$ .

NEW YORK CITY,  
September, 1902.

## A CHEMICAL METHOD FOR DETERMINING THE QUALITY OF LIMESTONES.<sup>1</sup>

BY ALFRED M. PETER.

Received October 20, 1902.

THE turnpike roads in the vicinity of Lexington, Kentucky, are built of the only stone which is conveniently within reach, namely: the limestone of the upper and middle beds of the Trenton formation. The character of the beds of this limestone is quite different at different levels, and it is common experience that the so-called "blue" layers are less valuable for any exposed construction than the "gray" because of their more rapid disintegration on exposure to atmospheric influences. Some beds which, when recently quarried, appear of fairly good quality are penetrated by thin layers of the blue material which disintegrate rapidly by weathering, causing the stone to separate into laminae of varying thickness. According to the writer's observation, the blue material is of two varieties; it may be quite shaly and moderately phosphatic or very phosphatic and not especially clayey, but it invariably contains easily soluble ferrous compounds and a small but very notable amount of organic matter which makes its presence known when the material is dissolved in dilute acids by the odor of petroleum imparted to the escaping gas and by the brown scum floating upon the liquid. The writer believes that the peculiar color of the so-called "blue" limestone is largely determined by the presence of a ferrous phosphate. He is of the opinion, also, that the rapid weathering down of blue material is due to the presence in it of easily oxidizing substances, such as ferrous compounds and organic matter, the oxidation of which is greatly favored by the greater porosity of this material, as compared with the gray limestone. The porosity of these blue limestones appears to increase with increasing amounts of phosphates and may in reality be dependent upon the presence of the minute spiral shell, *cyclora minuta* which, as has been shown by the writer and Professor A. M. Miller,<sup>2</sup> carries the phosphate. When this shell is present in very large numbers it gives to the rock a structure somewhat resembling that of chalk, though more compact. These soft limestones, and especially the shaly kind containing clay, also contain some finely granular pyrite which, by its oxidation, undoubtedly promotes disintegration.

<sup>1</sup> Read before the Cincinnati Section of the American Chemical Society, October 8, 1902.

<sup>2</sup> Eighth Annual Report Kentucky Agricultural Experiment Station, p. 25.

For the general character of the Trenton limestones of Central Kentucky reference is here made to Report A of the Kentucky Geological Survey, Vol. 2, pages 123-4. In the analyses there published of 18 samples of limestone from Trenton group in Bourbon, Clark, Fayette, Franklin, Madison, Mercer and Woodford counties, Kentucky, by Dr. Robert Peter, the silica and silicates insoluble in hydrochloric acid of 1.15 sp. gr. vary from 1.88 to 14.18 per cent., the average being 5.36 per cent., and the phosphoric acid ranges from 0.118 to 0.860, the average being 0.434 per cent. Later analyses by Dr. Robert Peter showed much higher percentages of phosphates in certain specimens.

If the writer's view of the causes of disintegration of these rocks is correct, a very good index of the relative stability of different samples could be obtained by measuring their relative amounts of easily oxidizable matters, phosphoric acid and clay or insoluble matters.

#### THE METHOD OF ANALYSIS.

The writer proposes, therefore, to dissolve the limestone in dilute sulphuric acid in the presence of a known amount of potassium permanganate and determine how much permanganate has been reduced during that process, after which the solution is to be used for the determination of phosphoric acid by a rapid volumetric method, and the insoluble residue, for the determination of the insoluble matter and clay.

*Determination of Oxidizable Matters.*—The method was actually carried out as follows: 1-gram portions of the finely powdered samples, previously dried at 100 C., were weighed into 250 cc. Erlenmeyer flasks, and 25 cc. of N/10 potassium permanganate solution measured into each and shaken until the powder was moistened; 100 cc. of a 10 per cent. sulphuric acid (110 cc.  $H_2SO_4$  of 1.84 sp. gr. + 1800 cc. of water) was then added and the flasks again shaken. If the color of the permanganate appeared to be nearly all discharged, as happened in some of the limestones examined, a second 25 cc. of permanganate solution was added at once. Two other flasks were charged with the same amounts of permanganate and sulphuric acid to serve as checks, upon the decomposition of the permanganate due to heat and acid alone. All the flasks were immediately placed upon a



boiling water-bath and allowed to remain there for half an hour, with occasional shaking, after which 30 cc. of  $N/10$  oxalic acid was run into each, or more, if necessary, and the flasks allowed to remain on the bath a few minutes longer, until the brown manganic compounds had entirely disappeared. It is well to adjust the quantity of oxalic acid added, so that there will be at least 8 or 10 cc. in excess of what is actually oxidized, as otherwise the disappearance of the manganic compounds will be slow. Where 25 cc. of permanganate had been used, 30 cc. of oxalic acid were enough, if the reduction by the limestone had been considerable, but not if this had been only slight. The flasks were then removed from the bath and the excess of oxalic acid titrated back with permanganate solution. The amount of permanganate reduced by the easily oxidizable matters in the limestone was thus ascertained, due allowance having been made in each case for the amount reduced in the control experiments.

The presence of pyrite in these limestones has already been mentioned and it was observed in several of the samples, after the acid had been poured on. After the titrations were finished, the residues were, in every instance, examined by means of a lens, before filtering, but in no case was any pyrite apparent. It is believed that it was completely oxidized. A qualitative test with finely powdered pyrite showed that it reduced the acid permanganate solution rapidly, even in the cold, but in a quantitative experiment with 0.02 gram of pyrite, 50 cc. of permanganate and 100 cc. of 10 per cent. of sulphuric acid, only about two-thirds were oxidized, probably because the mineral was not ground sufficiently fine.

The writer proposed to make a separate determination of the pyrite in these limestones by a rapid method based upon the reaction observed by A. Rollet<sup>1</sup> but time did not permit.

To ascertain whether one-half hour digestion with the sulphuric acid and permanganate was long enough to obtain the whole reducing effect of the samples, a set of duplicates was made upon six of the samples, digesting them one-half and one hour respectively. The results were substantially the same, as shown below.

Cubic centimeters permanganate solution reduced by 1 gram of sample (1 cc. permanganate = 0.00078 gram available oxygen).

<sup>1</sup> Ref. in *Am. Chem. J.*, 2, 69 to Dingler's *poly. J.*, 233, 124.

	Blank.	1.	2.	3.	4.	5.	6.	Blank.
1 hour digestion.	1.95	3.85	2.45	29.85	11.65	6.45	6.05	2.25
½ hour digestion	1.1	3.1	2.1	28.2	10.7	5.6	5.4	1.3
Gross difference.	0.85	0.75	0.35	0.65	0.95	0.85	0.65	0.95

As the average increase of decomposition in the blank experiments is 0.9 cc., it is evident, therefore, that the oxidation was complete in half an hour. Indeed it is probable that the reaction is practically complete in the cold, or that heating for a shorter time than one-half hour would suffice, but no experiments were made to test this supposition. It is noteworthy that, when the acid is poured upon the limestone, in the presence of permanganate, the petroleum-like odor is very slight and there is no floating carbonaceous matter observable, whereas, with the acid alone, these are both very evident, as already mentioned.

*Determination of Insoluble Matter and Clay.*—After the titration, a drop or two more of oxalic acid was added to remove traces of permanganate, and 10 to 15 cc. of hydrochloric acid of reagent strength (20 per cent) to retard crystallization of calcium sulphate, and the solutions filtered from the residues as quickly as possible. It was difficult to obtain a perfectly clear filtrate without too much waste of time, so a slight opalescence of the liquid from suspended clay was disregarded in most cases. The residues were washed, first with a little warm, dilute hydrochloric acid, finally with water, burned and weighed as total insoluble residue. A comparison of the amounts of insoluble residue obtained in the half-hour and one-hour digestion already described, shows only a very slight decrease by the longer digestion.

PER CENT. OF INSOLUBLE MATTER.

	1.	2.	3.	4.	5.	6.
½ hour digestion....	2.94	1.45	18.75	8.22	2.29	2.43
1 " " ....	2.88	1.48	(17.08)	8.05	2.25	2.42
Difference.....	0.06	—0.03	( 1.67)	0.17	0.04	0.01
Average.....	2.91	1.46	(17.92)	8.14	2.27	2.43

Some of the residue from the one-hour digestion of No. 3 was accidentally lost before weighing, so that the difference in this case is not really as great as it appears.

In order to separate the sand and clay, the residue obtained from a duplicate determination of the easily oxidizable matter was transferred, together with the filter, without burning, to a platinum dish of about 100 cc. capacity, and gently boiled with 10

cc. of concentrated sulphuric acid for several hours, the dish being covered with a watch-glass during the operation. A small amount of potassium nitrate was added to hasten the oxidation of the filter-paper. After cooling, about 50 cc. of water were added and the contents of the dish boiled a few minutes, allowed to settle, and filtered, leaving as much of the residue as possible in the dish.

After washing this residue, it was boiled with three successive portions of a saturated solution of sodium carbonate to separate soluble silica, thoroughly washed, burned and weighed. This weight was designated sand and the difference between this and the total insoluble residue previously determined was considered clay. Qualitative tests of some of these residues showed that they were not pure quartz sand, but still contained silicates, probably feldspathic in character, as a very notable amount of potassium was present.

*Determination of Phosphoric Acid.*—The phosphoric acid was determined by A. L. Emery's modification of the volumetric method of the Association of Official Agricultural Chemists.<sup>1</sup> For this purpose, half of the solution obtained by dissolving the limestone in the sulphuric acid permanganate was used. When it is not desired to weigh the insoluble matter, this solution may be used without filtering. An independent determination of phosphoric acid was made for comparison upon the first six samples by the same volumetric method, using the solution obtained by dissolving 0.5 gram of the sample in nitric acid. The results are given below and show a reasonable agreement between the two methods.

## PER CENT. OF PHOSPHORIC ACID.

	1.	2.	3.	4.	5.	6.
Solution in $H_2SO_4$ and $K_2Mn_2O_8$ ..	1.00	0.18	2.42	1.98	0.60	0.62
" " $HNO_3$ .....	1.02	0.14	2.32	1.80	0.54	0.48
Difference.....	—0.02	0.04	0.10	0.18	0.06	0.14
Average.....	1.01	0.16	2.37	1.89	0.57	0.55

The molybdic precipitates obtained from the sulphuric acid solutions were easier to filter and wash than those from the nitric acid solution, the latter showing a great tendency to run through the filters.

## DESCRIPTION OF THE SAMPLES.

In this investigation 18 samples of limestone were analyzed,

This Journal, 24, 895.

collected by the writer from stone in use upon roads near Lexington or from quarries which had been worked for such stone. The samples were chosen especially with reference to presenting the best, the worst and about the average quality of the material now actually in use for road construction in this locality. They may be described briefly as follows:

No. 1. Gray, crystalline, fossiliferous limestone; very hard; broken from an eight-inch ledge which appeared to have resisted the weather. From an old quarry on the Nicholasville road.

No. 2. Hard, gray, crystalline stone selected from a pile of broken stone on the roadside, Nicholasville road.

No. 3. Blue, slaty, soft stone, selected from the same pile as No. 2. It was already disintegrating, although it had only been exposed a few months.

No. 4. Blue limestone from the roadside; not as shaly as No. 3, but weathering in places to a soft pinkish material.

No. 5. Hard, gray, compact stone, selected from the road now in process of construction at the Lexington Fair Grounds. The superintendent of the Construction Company considers this the best stone for the purpose he has used about Lexington.

No. 6. Average of small pieces taken from the same road as No. 5.

No. 7. Hard, gray, crystalline stone, selected from a pile by the roadside on the Bates Creek pike.

No. 8. Thin, blue, slaty piece from the same pile as No. 7.

No. 9. Another slaty, blue piece from the same pile.

No. 10. Compact, hard, gray stone selected from the roadbed near the same place as No. 7.

No. 11. Average from the same place as the preceding, obtained by taking small pieces from the surface of the road where it had been exposed by washing; mostly blue limestone.

No. 12. Average of small pieces taken from a pile of crushed rock by the roadside on the Bryan's Station pike. The superintendent of the Construction Company states that the stone used on this pike is the worst he has met with about Lexington.

No. 13. Representative sample of the thin, soft, blue layers in the quarry on the Bryan's Station pike.

No. 14. Representative pieces from the thicker, soft, blue layers in the same quarry.

No. 15. Selected piece of the harder blue layers in the same quarry.

No. 16. Nearly white, very hard, concretionary masses occurring in the soft, blue layers in the same quarry.

No. 17. Thin, slaty layers from the same quarry. Disintegrate very rapidly.

No. 18. Selected piece from the hard layers in the upper part of the same quarry, which seem to have resisted weathering.

## RESULTS.

The results of the analyses were as follows, calculated as per cent. of the samples dried at 100° C.

	Number.	Oxygen consumed.	P <sub>2</sub> O <sub>5</sub> .	Sand.	Clay.	Total insoluble.
Tough, hard, compact stone, resisting weathering, mostly gray.	1	0.143	1.01	2.26	0.65	2.91
	2	0.048	0.16	1.34	0.13	1.47
	5	0.341	0.57	1.63	0.64	2.27
	6	0.318	0.55	1.76	0.66	2.42
	7	0.137	0.18	...	...	1.33
	10	0.133	0.22	...	...	1.50
	15	0.207	0.98	...	...	0.88
	16	....	0.20	...	...	4.15
	18	0.160	0.47	...	...	1.44
Average,		0.165	0.48	1.75	0.52	2.04
Highest,		0.341	1.01	2.26	0.66	4.15
Lowest,		0.048	0.16	1.34	0.13	0.88
Soft, porous or shaly stone, weathering rapidly, mostly blue.	3	2.120	2.37	7.73	10.19	17.92
	4	0.743	1.89	6.23	1.91	8.14
	8	0.952	1.90	17.43	7.64	25.07
	9	0.948	1.68	17.42	8.24	25.66
	11	0.666	0.96	4.20	4.08	8.28
	12	0.843	4.62	...	...	2.59
	13	0.710	6.24	...	...	2.06
	14	1.139	9.10	...	...	2.10
	17	2.044	4.52	12.53	10.23	22.76
Average,		1.129	3.70	10.92	7.05	12.73
Highest,		2.120	9.10	17.43	10.23	25.66
Lowest,		0.666	0.96	4.20	1.91	2.06

A study of these results shows that the soft, blue, rapidly weathering limestones are characterized by the presence of high percentages of easily oxidizable matter and phosphates, accompanied in the shaly kinds by a high percentage of insoluble matter containing a large proportion of clay. In three instances there is

some appearance of a deviation from this rule. Sample No. 1 was selected as being very hard and apparently resistant to weathering, nevertheless it contains 1 per cent. of phosphoric anhydride, which is more than the average for good limestone. However, the "oxygen consumed" is not large. In samples 5 and 6, taken from a road in process of construction, the material of which was considered very good, the "oxygen consumed," while not excessive, is distinctly larger than in most of the selected gray rock, and the phosphoric acid is over 0.5 per cent., or slightly above the average. However, the uniform character of this stone is shown by the close agreement between the figures obtained from the selected piece, No. 5, and the average sample, No. 6. On this account the favorable opinion as to its quality may be considered to have been confirmed by this test.

#### CONCLUSION.

The conclusion would seem justified that the limestone which consumes much more than 0.3 per cent. of oxygen and at the same time contains as much as 1 per cent. of phosphoric acid, more especially if it contains also several per cent. of clay, will disintegrate rapidly upon exposure to air and moisture and will be undesirable for road building or other exposed construction.

While this method of analysis has not been tried upon other rocks than the Trenton limestone, it is probably of much more general application, especially that part of it which takes into account easily oxidizable constituents of rocks.

The writer is indebted to Mr. S. D. Averitt of this laboratory for assistance in the determinations of phosphoric acid and sand and the weighing of the total insoluble matter.

KENTUCKY AGRICULTURAL EXPERIMENT STATION,  
LEXINGTON, KY., September 30, 1902.

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#### [CONTRIBUTIONS FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.] THE DETERMINATION OF ATMOSPHERIC CARBON DIOX- IDE BY THE WALKER METHOD.

BY A. G. WOODMAN.

Received October 30, 1902.

DETERMINATIONS of carbon dioxide in atmospheric air or in the air of rooms, where results must be obtained with a considerable degree of accuracy, are usually made by the well-known

Pettenkofer method in some form or other. While this method is convenient and for a long time has been the favorite, it is now quite generally recognized that it contains inherent sources of error which can be obviated only by the use of complicated apparatus and extreme skill in manipulation. That the method can be employed to obtain results of the highest degree of accuracy, has been shown by Letts and Blake<sup>1</sup> in an exhaustive study of the question. The refinements found necessary, however, place their modification out of consideration for ordinary use. A method which is comparatively simple and at the same time accurate has been proposed by Walker.<sup>2</sup> This method may be briefly outlined as follows:

To a definite volume of air, usually 1 to 2 liters, is added a measured amount of standard barium hydroxide, care being taken to avoid contact of the solution with the air. After the absorption of the carbon dioxide, the solution is filtered under reduced pressure through asbestos and the clear barium hydroxide received into a known excess of standard hydrochloric acid. The absorption vessel is rinsed out with water free from carbon dioxide. The excess of acid is then determined by titration with barium hydroxide.

The principal errors of the Pettenkofer method in its usual modifications, *viz.*, contact of the absorbing solution with the carbon dioxide of the air or the exhaled breath, action of the caustic alkali on the glass of the container, and the presence of small amounts of the precipitated barium carbonate, are thus avoided.

The work which has been carried out has been mainly the determination of most suitable conditions, such as the necessary time for absorption, the most suitable filtering media, etc. A series of tests on air free from carbon dioxide and on mixtures of known amounts covering a wider range than those described by Walker, has also been made. It will be unnecessary to detail all the preliminary experimental work made to acquire familiarity with the apparatus and facility in manipulation. Much work which was found later to be of little value will be omitted entirely from the discussion. The analytical work has been of necessity

<sup>1</sup> *Proc. Royal Dublin Soc.*, 9, 107 (1900).

<sup>2</sup> *J. Chem. Soc.*, 77, 1110 (1900).

carried on with considerable interruption and has extended over some time.

#### REAGENTS AND APPARATUS.

The standard solutions used have been N/50 hydrochloric acid, and barium hydroxide, approximately N/100, its exact strength relative to the acid being found daily by titration. It was found advantageous to use solutions of this strength, somewhat more dilute than those recommended by Walker, on account of the increased accuracy with air nearly free from carbon dioxide. The decreased range of usefulness is readily compensated by the employment of smaller samples of the impure air.

The preparation of the acid requires no special comment, it being standardized by gravimetric determinations as silver chloride and preserved in a hard glass bottle in the usual manner. The barium hydroxide, which was made up in quantities of 8 liters at a time, was preserved with especial care. The hard glass bottle containing it, placed on a high shelf so that the measuring apparatus could be filled directly by gravity, was heavily coated on the inside with barium carbonate. This was found as efficient as the paraffin used by Letts and Blake which seemed to have a tendency to flake off with changes in temperature. The bottle was closed by a rubber stopper with two holes, one of which carried the siphon tube dipping to the bottom of the bottle and supplying the measuring burette, while the other carried a fairly large glass T (Fig. 1). From one-half the horizontal arm of this projected a glass tube carrying the device for protecting the solution. This device is shown drawn on a somewhat larger scale in the same sketch. The horizontal tube entered the T-tube far enough to support the apparatus. Connection was made by a closely fitting rubber tube. The longer tube, reaching nearly to the bottom of the test-tube, carried a fairly good sized "calcium chloride tube" which contained soda-lime, enclosed in the usual manner by plugs of cotton. The test-tube contained 5 to 10 cc. of dilute (about N/50) caustic potash colored with phenolphthalein, the whole serving to indicate the efficiency of the soda-lime. From the other end of the horizontal arm of the T projected in the same way a long tube bent at right angles fitting by a rubber stopper into the top of the burette, thus making the whole a closed system,



much after the manner of Blochmann.<sup>1</sup> Any air entering the

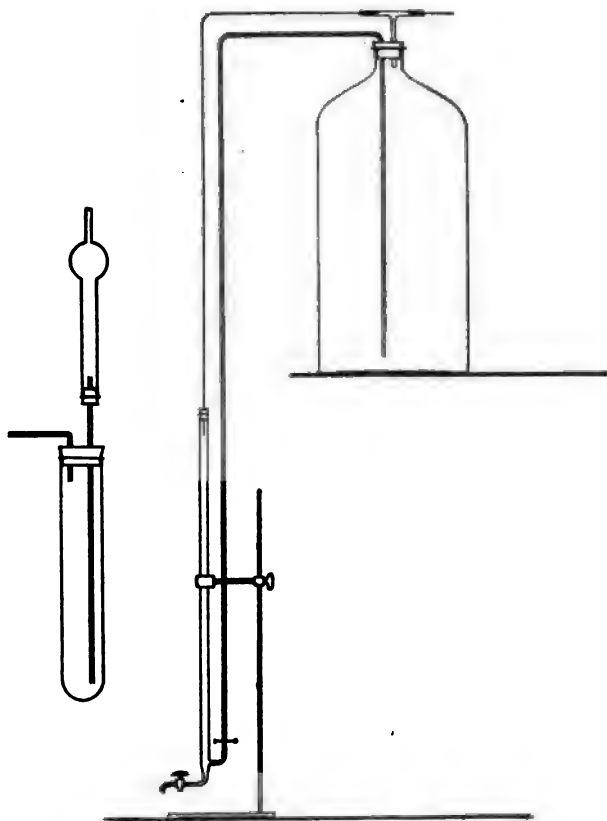


Fig. 1.

bottle when the solution is drawn from the burette or when the burette is filled again must have come through the protecting apparatus. This will be found efficient, if care is taken in the selection or preparation of the soda-lime.<sup>2</sup>

The burette used for the barium hydroxide was a glass-stoppered one, differing somewhat from the ordinary form. The lower portion below the graduations was narrowed and bent at right angles. This horizontal part was fitted with an ordinary glass stop-cock. This gave no trouble when kept well vaselined.

<sup>1</sup> *Ann. Chem.* (Liebig), 237, 39 (1887).

<sup>2</sup> Directions for preparing a good quality of soda-lime are given by Benedict and Turner, *this Journal*, 21, 396 (1899).

The tip of the burette was kept covered with a little rubber cap when not in use to prevent clogging from the formation of carbonate. The apparatus could easily be arranged with a special pipette for the delivery of a definite charge of baryta solution but this was not considered worth while for the purpose of testing the method. It was not found necessary to coat the inside of the tubes or the measuring apparatus with paraffin. The solution was always drawn from the burette and replaced by fresh if it had stood for any time. The apparatus as described was found to be remarkably efficient for the preservation of barium hydroxide. While determinations of the strength of the solution by titration against the hydrochloric acid were made every day, it was found as a matter of fact that the solution underwent no appreciable change during a month or so.

The bottles used for the collection of samples were of hard glass, some of 2-liters capacity, others of 1-liter, the exact volume being determined in each case to a cubic centimeter. Some of the bottles were fitted with glass tubes and stop-cocks as described by Walker; in others the stop-cock was replaced by a bit of rubber tubing and a Mohr pinch-cock which answers the purpose quite well though not so conveniently as the glass stop-cock. The bottles were used both plain and coated with paraffin.

The apparatus used for filtering off the barium carbonate, being made from material at hand, differed somewhat from that recommended by Walker. It may therefore need a word of explanation.

To the base of a ring-stand was firmly clamped an ordinary filter-bottle of about 250 cc. capacity closed by a rubber stopper with two holes. Through one of these passed a tube leading to the suction pump, through the other the tube of a Gooch filtering funnel, the upper part of which was cut off so that the remainder above the constriction was about an inch long. The tip projecting into the bottle was bent so that the liquid should flow down the side and not spatter. A rather close coil of stout platinum wire placed above the narrow portion served as a support for the asbestos filter or could be removed if it was desired to use cotton instead. In the upper part of the tube was tightly fitted a rubber stopper through which passed a narrow glass tube extending to within one-eighth inch of the asbestos layer and provided above

the stopper with a stop-cock. Connection was made with the

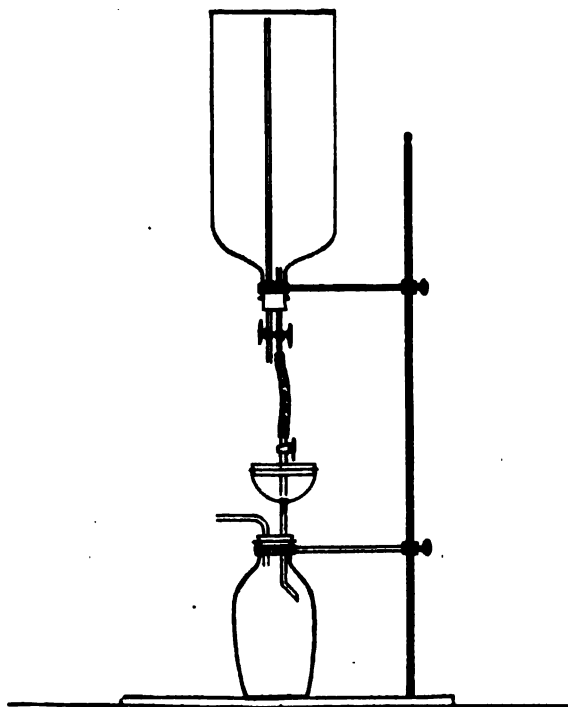


Fig. 2.

short tube of the inverted bottle by means of a rubber tube.

All rubber stoppers and connections with which the solutions could possibly come in contact were cleaned by boiling in a 5 per cent. potash solution, washed, and boiled in dilute bichromate and sulphuric acid mixture, rubbed thoroughly and washed until free from acid.

#### NOTES ON THE PROCEDURE.

The procedure adopted follows in its general outlines that of Walker but since it was found at an early stage of the work that success depended on a close observance of details in manipulation it might be well to mention the precautions found useful.

*Collection of Samples.*—With such small bottles, this is an easy matter. Any method may be used which secures a complete exchange of the air and prevents contamination with the breath.

It is better for this reason to draw the air out of the bottle than to force it in. For the present purpose, samples for comparison were collected by aspirating the air at a rapid rate through several bottles connected tandem, the air entering through the longer tube and leaving by the shorter one so as to sweep the bottle out completely. The air was drawn through usually for fifteen to thirty minutes, then the bottles allowed to remain connected for a time that the air might be equally distributed. No samples were collected at a temperature higher than that at the time of analysis and they were always allowed to come to the higher temperature of the laboratory so that there was always an outward pressure when the bottle was opened. It is, of course, unnecessary to use dry bottles for collecting the samples.

*Absorption of the Carbon Dioxide.*—It was found best instead of trying to force the alkali solution entirely below the level of the stop-cock by squeezing the rubber tip, to pinch it and then insert a bit of glass rod about an inch long as a plug to keep out the air. The absorption was usually carried on for thirty minutes.

*Filtering off the Barium Carbonate.*—25 cc. of the hydrochloric acid was used and the bottle was rinsed with 100-150 cc. of prepared "wash water"—made as suggested by Walker, by adding 1 cc. of a 10 per cent. barium chloride solution and 3 drops of phenolphthalein, then titrating with barium hydroxide to a faint permanent pink. Rinsing three times, using 25-30 cc. of wash water each time, was generally sufficient. One advantage of paraffined bottles is that they drain more completely and hence the washing is more readily performed. The preparation of this wash water was usually carried out during the absorption and the water kept in stoppered flasks. Some of the water should also be used to wash down the filter tube.

Equally good results were obtained by using 100 cc. of distilled water which had had air free from carbon dioxide passed through it in a fairly rapid stream for two hours and then been preserved out of contact with the air. This was usually done on a considerable quantity which was kept in a hard glass bottle and drawn off through a siphon tube as required for use.

*The Titration.*—The acid solution was transferred from the filter bottle to a 6-inch porcelain dish for titration. Barium hydroxide was added to the production of a distinct pink color,

the solution then returned to the bottle and finally poured again into the dish. One or two drops of the alkali solution usually sufficed to finish the titration.

#### EXPERIMENTAL.

*Standardization of the Barium Hydroxide.*—This was the first problem that presented itself. The natural method would seem to be titration directly against the hydrochloric acid, using the indicator used in the actual determination; but since "neutralized water," that is, distilled water in which the dissolved carbon dioxide had been neutralized with baryta, was to be used in the determination, it seemed on the other hand, that the standardization should be carried out under similar conditions as regards dilution. Again, since barium chloride has been added to the wash water to assist in the separation of the barium carbonate and it has passed through a filter, the carbon dioxide may be considered removed. Why, then, should not equally good results be obtained, with less trouble, by determining the amount of carbon dioxide in a given volume of water and applying a correction for the amount of wash water used? Still another method was by the use of "purified water," by which is meant distilled water with the carbon dioxide removed as previously described.

These four methods, then, have been tried: (a) Direct standardization; (b) using 150 cc. of "neutralized water" to dilute the hydrochloric acid solution; (c) applying a correction for the amount of carbon dioxide in the diluent water; (d) using 100 cc. of "purified water."

The results are given in Table I, the value calculated being that of the barium hydroxide in terms of the standard acid.

TABLE I.—METHODS OF STANDARDIZATION.

a.	b.	c.	d.
0.5175	0.5225	0.4855	.....
0.5147	0.5170	.....	.....
0.4832	.....	.....	0.4829
0.4832	.....	.....	0.4831
0.4796	.....	.....	0.4794
0.4798	.....	.....	0.4803
0.4924	0.5048	.....	0.4928
0.4948	0.5077	0.4808	0.4945

The values obtained with purified water and by direct standardization were nearly the same and are undoubtedly the correct

ones. Distilled water gave values which were too low, even when a correction was made for the carbon dioxide that it contained. The results with neutralized water, on the other hand, which might be expected to agree with those for purified water, were invariably high. This is probably due to the barium carbonate which has not been removed, since experiments made with a small flask exhausted of its air and fitted with stop-cocks and the filtering arrangement gave results identical with the direct standardization.

The method of standardization finally adopted was either the direct method or the use of 100 cc. of purified water, the bottle being rinsed out with 150 cc. of neutralized water, for which no allowance was made. That is to say, none was poured directly into the filter bottle but all that was used passed through the filter.

*The Filtering Medium.*—Tests were made using asbestos as the filtering medium and also using cotton. It was found rather more convenient to use a bit of absorbent cotton packed into the stem of the funnel tube in place of the platinum coil. A comparison of the two showed that for ordinary work either medium could be employed but that the cotton gave slightly higher results, as might be expected from the results published by Reiset<sup>1</sup> on the filtration of baryta water through paper.

TABLE II.—FILTERING MEDIA.

Source of air.	Filter.	Time. Minutes.	CO <sup>2</sup> in 10,000.
Outdoors	Cotton	30	3.26
"	Asbestos	30	3.18
Room	Cotton	30	4.05
"	Asbestos	30	4.01
"	Cotton	30	4.10
"	Asbestos	30	3.93
"	Cotton	30	3.99
"	Asbestos	30	4.01

*Time Necessary for Absorption.*—It is possible to carry out the absorption of the carbon dioxide in fifteen minutes, as Walker states, by agitating the bottle almost constantly. In most cases, however, it would be better to continue the absorption for a little longer time, say for twenty to thirty minutes. A longer time than this is unnecessary and in the case of bottles which are not paraffined it is undesirable.

<sup>1</sup> *Ann. chim. phys.*, [5], 26, 155 (1882).

TABLE III.—TIME NECESSARY FOR ABSORPTION.

Source of sample.	Time of shaking. Minutes.	CO <sub>2</sub> in 10,000.
Room	15	3.89
"	30	3.99
"	60	3.95
"	60	3.93

*Action of the Alkali on the Glass of the Bottle.*—The tests which were made confirmed Walker's conclusion that in the short time necessary for absorption the solvent action of the alkali on the glass is negligible.

TABLE IV.—ACTION OF THE ALKALI ON THE GLASS.

Source of sample.	Paraffined bottle?	Time. Minutes.	CO <sub>2</sub> in 10,000.
Room	No	30	3.68
"	"	30	3.63
"	Yes	30	3.75
"	"	30	3.78
"	No	30	4.84
"	Yes	30	4.78
"	"	30	4.81

*Tests on Air Free from Carbon Dioxide and on Known Mixtures.*—To obtain a rigid test of the method, determinations were made on air free from carbon dioxide and on similar samples to which a known amount of the gas had been added. The blank determinations were made both on the vacuous bottles from a previous determination and on samples in which air free from carbon dioxide was drawn through the bottles until the original air was entirely displaced. This was determined by passing the air from the bottle through a saturated solution of baryta and in no case was the sample used if the clear solution showed any turbidity when the air was drawn through it at a rapid rate for twenty minutes.

In the tests on known amounts of carbon dioxide, the vacuous bottles were also employed. The carbon dioxide, which was generated by heating magnesium carbonate, was measured over mercury in capillary tubes and added through the shorter tube of the bottle.

TABLE V.—TESTS ON AIR FREE FROM CARBON DIOXIDE.

Filter.	Wash water used.	Standardisation.	CO <sub>2</sub> in 10,000.
Cotton	Neutralized	Direct	—0.14
"	Purified	"	0.06
"	Neutralized	"	0.00
"	Purified	"	0.18
"	"	Purified water	0.01
"	Neutralized	Direct	0.07
"	Purified	"	—0.02
"	Neutralized	"	—0.06
None	"	"	—0.01
Cotton	"	"	0.01
"	"	"	—0.02
"	"	"	0.01
Asbestos	"	"	—0.02
"	Purified	"	—0.01
"	Neutralized	"	0.01
"	Purified	"	0.00
"	"	"	0.01
"	"	"	0.01
"	Neutralized	"	0.03
"	"	"	—0.07
"	"	"	0.05
"	"	"	—0.01
"	"	"	0.03

TABLE VI.—TESTS WITH KNOWN AMOUNTS OF CARBON DIOXIDE.

Cc. added.	Temperature.	Bar. Inches.	Cc. N. T. P.	Volume found.
0.852	25.8°	29.85	0.752	0.744
0.841	27.0	30.07	0.742	0.715
1.33	25.0	29.97	1.182	1.182
1.28	24.8	29.96	1.139	1.16
2.011	25.0	29.92	1.784	1.802
1.23	25.3	29.92	1.090	1.075
2.221	25.4	29.92	1.967	2.01
2.158	25.3	29.89	1.972	1.945
1.37	21.2	30.24	1.285	1.286
1.325	21.8	30.24	1.240	1.273
2.074	21.8	30.23	1.941	1.922
1.877	23.0	30.18	1.746	1.708
0.878	23.6	30.18	0.815	0.791
0.995	23.6	30.18	0.924	0.919
1.057	22.6	....	0.990	0.996

## CONCLUSIONS.

The results obtained confirm Walker's statement that the method is accurate under ordinary circumstances to 0.1 part in



10,000. With careful work and attention to details it should be accurate to a much greater degree than this, certainly to 0.03 part. It can hardly be said, however, that amounts of carbon dioxide varying from 0 to 40 parts in 10,000, can be determined without modification of the method. The barium hydroxide must always be present in considerable excess, a condition which is most readily attained by the use of a smaller sample of bad air. With a little practice, the method was found to be rapid and easy of execution and preferable to the Pettenkofer method.

BOSTON, MASS.,

October 28, 1902.

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## LIQUID BATHS FOR MELTING-POINT DETERMINATIONS.

BY HEYWARD SCUDDER.

Received November 28, 1902.

A MIXTURE prepared by boiling together for five minutes seven parts by weight of sulphuric acid (sp. gr. 1.84) and three parts by weight of potassium sulphate remains a transparent liquid at ordinary temperatures and can be heated up to  $325^{\circ}$  without boiling. If the proportions are changed to six parts by weight of acid and four parts of the sulphate the mixture forms a soft mass at ordinary temperatures (though after boiling and then cooling down it will usually remain liquid for half an hour or more) melting from  $60^{\circ}$ - $100^{\circ}$  and boiling above  $365^{\circ}$ . Acid potassium sulphate can be used instead of potassium sulphate. In this case the amount should be calculated to give the same ratio of potassium sulphate to sulphuric acid.

These mixtures are self-clearing and remain permanently white (turning slightly yellowish at about  $230^{\circ}$ ) unless much organic matter gets in. They can be cleared, if brown, by boiling with a few drops of concentrated nitric acid or with a small crystal of potassium nitrate. The vapor is so slightly acid that the capillary can always be fastened to the thermometer by a rubber band, provided the band is 1 to 2 cm. above the surface of the bath. Platinum wire need never be used. In preparing the bath, after the potassium sulphate has melted the two layers should be mixed or explosive boiling may occur.

Most melting-points given accurately are below  $325^{\circ}$ . The first mixture is therefore suitable for all ordinary purposes. It

does not have to be renewed frequently as does the ordinary sulphuric acid bath nor does it become permanently discolored as does paraffin after short use, even though prepared by distillation under diminished pressure.

If the bath has solidified (which happens sometimes under unknown conditions though very rarely), boiling for a minute or two will bring it back to its original condition. If it has not been used for a number of weeks, it should be boiled for a minute or two before using for temperatures above  $300^{\circ}$ .

For temperatures from  $360^{\circ}$  to  $600^{\circ}$  Mr. Booth, working under the direction of Dr. Mulliken of this laboratory, has found that the most satisfactory bath is fused zinc chloride. This melts to a clear transparent liquid at about  $250^{\circ}$ . After use it must be poured out on a tile while liquid, since it expands on solidification and will crack any flask or beaker in which it is allowed to grow cold. It can be cleared from organic impurities by heating with a small crystal of potassium nitrate. Unless the zinc chloride used is pure, the bath will gradually become opaque after a short time and can not be made transparent again.

The temperatures given here are uncorrected. They were obtained in a melting-point apparatus made by inserting a test-tube in a round-bottomed flask (150-250 cc.). The bottom of the tube is about 1 cm. from the bottom of the flask. The bath is placed both in the test-tube and in the flask. In this apparatus fresh sulphuric acid (sp. gr. 1.84) can be used up to  $280^{\circ}$ - $300^{\circ}$ . In using the sulphate mixtures, if the upper part of the tube becomes cloudy from a film of solid, it can be cleared by boiling with a little concentrated nitric acid. In using such an apparatus it is not safe to heat it much above the temperatures given here for the various baths since the boiling is apt to start very violently. It is safe to heat it till large bubbles begin to rise moderately frequently.

When these baths are used in open beakers, it is not possible with sulphuric acid or the sulphate mixtures to obtain temperatures as high as those previously mentioned, without having disagreeable amounts of acid vapor given off. The zinc chloride bath can be used in a beaker up to about  $600^{\circ}$ .

The sulphate mixtures seem to contain some compound in a persistent state of supersaturation. Although possessed of considerable oxidizing power when hot, it is a curious fact that they

are markedly less caustic than hot concentrated sulphuric acid when dropped on the skin.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
November, 1902.

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## THE PREVENTION OF BUMPING.

BY HEYWARD SCUDDER.

Received November 28, 1902.

A SINGLE glass capillary tube when used according to the following directions will stop most cases of bumping that occur in ordinary laboratory work. The method is simple, effective and introduces into the liquid no foreign substance except glass and one small bubble of air. In order to carry it out successfully the following details of procedure must be carefully observed.

The origin of the use of a capillary is obscure. The earliest published reference that I have found is by Gernez.<sup>1</sup> Since these references are only incidental and therefore difficult to find, it is quite possible that there may be an earlier one. I have tried all the methods published (most of which are only for special cases), and have found none so simple or of such wide application as the one presented here.

The capillary is made by drawing out a piece of glass tubing until the internal diameter is about 0.5 to 1 millimeter. A seal is then made by holding the tube horizontally in the edge of the flame of a Bunsen burner, until the walls have melted together. The tube is bent, if necessary, or held horizontally till cold. For most purposes the seal should be about 1 cm. from the open end of the tube. The tube is cut off at the desired length and the other end sealed to prevent the entrance of liquid. When cold, the tube is placed open end down in the liquid to be boiled. The open end should rest on the bottom of the vessel containing the liquid and should remain there during use. When liquids of high specific gravity are being boiled, it is necessary, therefore, to have the capillary so heavy that it will not be thrown off the bottom. This weight can be obtained by drawing out the tube from which the capillary is made only near the seal, or by using a very thick walled tube.

In a general way the theory of the action of such a tube is that

<sup>1</sup> *Compt. Rend.*, 86, 472.

when heated the air in the capillary expands and passes through the liquid in bubbles. The vapor of the liquid gradually replaces the air and the stream of bubbles is continuous as long as the temperature around the capillary is at the boiling-point of the liquid. This constant bubbling prevents superheating and consequent explosive boiling. It is apparent that the size of the bubble will depend chiefly on the width of the capillary. This should vary with the nature of the liquid. For liquids of low boiling-point or for frothing liquids a narrow capillary is best, while for heavy liquids a wider capillary (even as wide as 5 mm. internal diameter) is more suitable.

When boiling with a return condenser, the seal of the capillary *must* be below the surface of the liquid. If the seal is above the surface, cold drops falling back from the condenser will strike the capillary and cause condensation of the vapor inside it, thus stopping the stream of bubbles. To prevent displacement, the capillary should be of such a length that the upper end reaches nearly to the top of the neck of the flask. When the liquid is in a thin broad layer the capillary should be bent at the seal so as to be parallel or nearly parallel to the bottom of the flask. In boiling liquids in a test-tube, care must be taken that the heat is applied at the bottom of the tube. When a solid is being dissolved, or when in the course of a reaction a solid is being precipitated out of solution, the capillary should be examined from time to time to see that the end has not become clogged.

The capillary is useless, if completely filled. Therefore it must be cold and empty when placed in the liquid. Care should be taken (especially in the case of liquids that usually bump badly) to protect the flame from drafts, so that the temperature of the liquid shall not temporarily fall below the boiling-point, allowing the capillary to fill.

Other minor changes and precautions may be advisable at times, but it will be found that they depend on the following principles. The capillary must never be allowed to become filled with liquid. The greater the amount of air there is to drive out (depending on the width of the capillary and the distance from the seal to the open end), the longer will it take to get a rapid stream of bubbles of vapor of the liquid. The greater the distance from the seal to the open end, the longer will it take to fill the capillary on cooling.

This method has been in successful use in these laboratories for nearly a year. By its use it is possible to saponify esters by boiling with a 50 per cent. solution of potassium hydroxide (using a return condenser) or to boil concentrated sulphuric acid in a test-tube, without any bumping. Only two cases have been met with in which bumping persisted after the capillary was introduced. Both were reactions carried out with a return condenser. Although the bumping continued, it was so greatly lessened that the liquid was not thrown out of the upper end of the condenser and there was no danger of having the flask broken.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
November, 1902.

[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS  
INSTITUTE OF TECHNOLOGY.]

# THE EQUIVALENT CONDUCTIVITY OF THE HYDROGEN ION DERIVED FROM TRANSFERENCE EXPERI- MENTS WITH HYDROCHLORIC ACID.

BY A. A. NOYES.

Received November 17, 1902.

(SECOND PAPER.)

IN a previous communication<sup>1</sup> bearing the same title made by A. A. Noyes and G. V. Sammet three series of determinations of the transference-numbers for  $\frac{1}{60}$  molar hydrochloric acid, at 10°, 20°, and 30°, respectively, were presented, from which by combination with the fairly accurately known values for the conductivity of the chlorine ion, the following ones for that of the hydrogen ion were obtained.

L	10°.	18°.	20°.	25°.	30°.
$\Lambda$	288.7	329.8	340.0	364.9	389.1

These values are 4 to 6 per cent. higher than those derived by Ostwald and Kohlrausch through a consideration of the change of conductivity of strong acids with the dilution. It was not considered possible that this divergence could arise from experimental errors in the transference determinations; but it was suggested that it might be due, at any rate in part, to a difference in the transference-numbers of the acid at extreme dilution and at the investigated dilution of 60 liters. To test this possibility, a new series of determinations has been made at 20° with an approxi-

<sup>1</sup> This Journal, 24, 944 (1902).

mately  $1/_{180}$  molar acid; and it is the purpose of this article to communicate the results. In this investigation I have been ably assisted by Mr. Raymond Haskell.

The method employed was substantially identical with that described in the previous article. The acid used was prepared from pure salt and sulphuric acid, washed with water, absorbed in a little pure water, and diluted with water having a conductivity of  $1.5 \times 10^{-6}$  reciprocal ohms. Three separate solutions, numbered 10, 11 and 12 in the table, were employed. These yielded respectively 0.7870, 0.7815, and 0.8240 milligram AgCl per gram of solution.

The data are given in detail in the following table, which is arranged like those previously published. The headings are for the most part self-explanatory. The content is always expressed in milligrams AgCl per gram of solution. The silver precipitated in the voltameters is also given in milligrams. The "transference-numbers" of the table are the actual values for the anion multiplied by 1000. The letters in the third column have the following significance:  $K$  = cathode portion;  $A$  = anode portion;  $M_K$  and  $M_A$  the middle portions adjoining these, respectively;  $M$ , the middle portion of all, lying between the last two.

$1/_{180}$ -MOLAR HCL AT 20°.									
Expt. No.	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in voltameters.	Transference number.
33	10	$K$	346.42	272.6	223.7	-48.9	-48.9	217.2	169.4
		$M_K$	210.26	165.4	165.2	- 0.2	.....	217.4	....
		$M$	177.44	139.6	138.1	- 1.5	.....	217.1	....
34	11	$K$	343.00	268.1	230.7	-37.4	-37.4	168.4	166.9
		$M_K$	142.68	111.5	111.7	+ 0.2	.....	168.7	....
		$M$	163.00	127.4	127.1	- 0.3	.....	168.7	....
35	11	$K$	340.56	266.2	229.3	-36.9	-36.9	167.1	166.3
		$M_K$	160.37	125.3	125.5	+ 0.2	.....	167.2	....
		$M$	168.81	131.9	130.8	- 1.1	.....	167.4	....
36	11	$K$	356.44	278.6	237.5	-41.1	-41.1	186.1	166.4
		$M_K$	160.64	125.5	125.5	$\pm$ 0.0	.....	186.0	....
		$M$	183.78	143.6	140.9	- 2.7	.....	185.8	...
37	11	$K$	349.28	273.0	234.8	-38.2	-38.2	172.0	167.2
		$M_K$	160.89	125.7	125.5	- 0.2	.....	171.8	....
		$M$	187.42	146.5	142.5	- 4.0	.....	172.1	....
		$A$	487.95	381.4	424.1	+42.7	+38.7	....	169.3

Expt. No.	Solution No.	Portion.	Weight of portion. Grams.	Initial content.	Final content.	Change in content.	Total change in content.	Silver in volta-meters.	Transference number.
38	12	<i>K</i>	319.12	263.0	221.8	-41.2	-41.2	185.0	167.7
		<i>M<sub>K</sub></i>	162.63	134.0	133.7	- 0.3	.....	185.0	....
		<i>M</i>	177.87	146.6	142.2	- 4.4	.....	185.1	....
		<i>A</i>	451.47	372.0	417.4	+45.4	+41.0	....	166.8
39	12	<i>K</i>	323.36	266.5	232.4	-34.1	-34.1	155.8	164.6
		<i>M<sub>K</sub></i>	136.82	112.7	112.6	- 0.1	.....	156.0	....
		<i>M</i>	169.80	139.9	138.3	- 1.6	.....	156.0	....
		<i>A</i>	451.46	372.0	410.9	+38.9	+37.3	....	180.0
40	12	<i>K</i>	305.85	252.0	210.1	-41.9	-41.9	188.0	167.7
		<i>M<sub>K</sub></i>	156.41	128.9	128.6	- 0.3	.....	188.3	....
		<i>M</i>	181.01	149.2	143.3	- 5.9	.....	188.1	....
		<i>A</i>	431.19	355.3	403.3	+48.0	+42.1	....	168.5
41	12	<i>K</i>	306.64	252.7	216.9	-35.8	-35.8	167.9	160.5
		<i>M<sub>K</sub></i>	156.91	129.3	129.5	+ 0.2	.....	168.0	....
		<i>M</i>	177.42	146.2	143.4	- 2.8	.....	167.9	....
		<i>A</i>	445.75	367.3	407.1	+39.8	+37.0	....	165.9
42	12	<i>K</i>	309.99	255.4	219.2	-36.2	-36.2	163.4	166.4
		<i>M<sub>K</sub></i>	162.39	133.8	133.6	- 0.2	.....	163.9	....
		<i>M</i>	172.73	142.3	139.3	- 3.0	.....	163.8	....
		<i>A</i>	453.88	374.0	414.2	+40.2	+37.2	...	170.9

The transference numbers are summarized in the following table. The values marked with an asterisk were omitted in the calculation of the mean.

$\frac{1}{100}$ -MOLAR HCL AT 20°.

Expt. No.	Cathode.	Anode.
33	169.4	....
34	166.9	....
35	166.3	....
36	166.4	....
37	167.2	169.3
38	167.7	166.8
39	164.6	180.0*
40	167.7	168.5
41	160.5*	165.9
42	166.4	170.9
Mean, 167.0		168.3
a.d., 0.9		1.5
A.D., 0.3		0.7
Final mean, 167.1		
A.D., 0.3		

The agreement of the cathode values among themselves is nearly as close as it was with the  $1/_{60}$  molar solution (where the a.d. was 0.8). The change in content of the adjoining portion  $M_x$  is also very small, mostly 0.2 mg. or less, and has opposite signs in different experiments. Even if this were added to the change in the cathode portion, it would increase the mean of the transference values by only 0.2 per cent. The anode values are much more discordant than the cathode values, owing to the more difficult manipulation involved in the preparation of the anode portion for analysis.<sup>1</sup> Nevertheless, the agreement of their mean with that of the cathode values within 0.8 per cent. is a confirmation of the substantial accuracy of the latter.

The final mean derived from the earlier determinations at 20° with  $1/_{60}$  molar solutions was 167.43 (A.D., 0.25). This agrees with the final mean of the present determinations (167.1; A.D., 0.3) at 20° with  $1/_{180}$  molar solutions within 0.25 per cent. (and within the limits of the sum of the A.D.'s). Hence it is justifiable to conclude that the transference-number of hydrochloric acid does not change appreciably with increase of the dilution after that of 60 liters is reached. The equivalent conductivities of the hydrogen ion derived in the previous article and summarized at the beginning of this one were therefore not vitiated by this assumption, which was made in their deduction.

The deviation between these values and those derived by extrapolation from the conductivities of acids still requires explanation. Whether it can be due to error in the estimate of the effect of the impurities of the water on the conductivities at great dilution could probably be determined through an investigation of that effect. Such an investigation will be undertaken in these laboratories.

BOSTON, November, 1902.

<sup>1</sup> In the first four experiments the anode results had to be rejected, owing to the use in the process of a large and indefinite amount of ammonium hydroxide, which was afterwards found to contain an appreciable quantity of chloride. In the later experiments a smaller and definite quantity of ammonia was used, and its chlorine-content determined and subtracted.



## ON THE COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID AND OF SILICA.

BY F. P. VEITCH.

Received November 23, 1902.

IN some of the field work of this bureau the analysis of drainage waters and of water extracts of soil is required daily. For this purpose the usual gravimetric processes are deemed impracticable on account of the time required, and it has been necessary to use more rapid volumetric, colorimetric, and photometric methods.

The writer suggested, and in the spring and early summer of the past year made an examination of, some known rapid colorimetric methods for the determination of phosphoric acid and of silica in these soil solutions. Incidentally, as the presence of iron in considerable amounts introduces errors in the determination of phosphoric acid, the rapid methods for the detection and estimation of minute quantities of iron have received some attention. As these latter methods have been thoroughly worked out and are quite well known, but passing reference need be made to them here.

For the estimation of phosphoric acid, the method described by Lepiere<sup>1</sup> and later studied in more detail by Woodman and Cayvan<sup>2</sup> promised to be the most rapid and to present the fewest difficulties in its manipulation.

For the adaptation of this method to the analysis of soil solutions, the influence of other compounds, both organic and inorganic, must be eliminated or determined. It was found that turbidity, organic matter where it produced a colored solution, ammonia salts in large amounts, iron salts in small amounts, dissolved silica and filter-paper introduce errors which are not negligible.

### REMOVAL OF SUSPENDED MATTER.

Turbidity may be removed by filtering through a Chamberland filter, which of course removes some of the phosphoric acid from the first runnings (see Table VIII). It may also be quite largely, sometimes completely, removed by evaporation to dryness

<sup>1</sup> *Bull. Soc. Chim.*, 18, 1213 (1896).

<sup>2</sup> *This Journal*, 23, 96.

and filtering; or it may be corrected for by matching the standard phosphomolybdate solution against the turbid solution and subtracting this reading from the final readings. None of these procedures is perfectly satisfactory, but nothing better has yet been devised. All have been used here, according to the difficulties presented. Where filtration will remove all suspended matter, this procedure is to be preferred, but as this cannot always be accomplished, the Chamberland filter or evaporation must be resorted to.

In the work about to be described the reagents were prepared as directed by Woodman and Cayvan<sup>1</sup> and were free from interfering substances. The same lot was used throughout the work, and all work was done at from 18°-22° C., the standard and the unknown solution being of course at sensibly the same temperature.

#### REMOVING ORGANIC MATTER.

Organic matter which colors the solution at all must be removed or it must be corrected for as above described, before reliable readings can be made. To accomplish this, two methods were tried: treatment with aqua regia, and ignition with magnesium nitrate. Several treatments with aqua regia were required to insure the destruction of all organic matter, after which the solutions were carried to dryness, taken up with water and 2 cc. nitric acid and compared in a reflecting colorimeter. The following readings were obtained:

TABLE I.

	Amount $P_2O_5$ added. Parts per million.	Amount $P_2O_5$ recovered. Parts per million.		Amount $P_2O_5$ added. Parts per million.	Amount $P_2O_5$ recovered. Parts per million.
1	1.0	1.0	4	5.0	4.3
2	2.0	1.1	5	7.0	6.1
3	3.5	2.4	6	9.0	7.1

We see that there is considerable loss of phosphoric acid from this concentrated aqua regia solution, a fact previously pointed out by Woodman and Cayvan.

Other phosphate solutions were then treated with magnesium nitrate free from silica, evaporated to dryness with nitric acid, and ignited in a porcelain dish until all carbon was burned off. The residue was then taken up with water and nitric acid, and compared with the standard solution.

<sup>1</sup> *Loc. cit.*

TABLE II.

	Amount $P_2O_5$ added. Parts per million.	Amount $P_2O_5$ recovered.		Amount $P_2O_5$ added. Parts per million.	Amount $P_2O_5$ recovered.
1	1.0	1.0	8	3.0	2.7
2	2.0	1.8	9	1.0	1.0
3	4.0	3.7	10	5.0	5.2
4	6.0	5.9	11	10.0	10.0
5	8.0	7.9			
6	9.0	9.2			
7	10.0	9.9			
				Average loss, 0.06	

The loss here is quite small, being as a rule within the limit of error of the reading. From these experiments it appears that the organic matter may be satisfactorily removed without loss of sensible amounts of phosphoric acid by ignition with magnesium nitrate and subsequent evaporation with nitric acid.<sup>1</sup> It may be said, however, that when the color due to organic matter is not greater than 0.2 to 0.3 part per million, it is hardly worth while to remove the organic matter, as a correction may be made for it by reading the color due to organic matter against the standard, and correcting the final reading by the reading thus obtained.

The volatility of phosphoric acid upon evaporation of these water solutions is at first sight rather startling to analysts, and while there is not the slightest doubt that it does take place from solutions of phosphoric acid<sup>2</sup> and from disodium phosphate solutions, there appears to be no reason to think that it occurs from solutions containing sufficient bases to form the normal phosphates. In no case has the writer obtained a loss from solutions of this character. As phosphates dissociate readily, it seems possible that water extracts of soils may contain occasionally some free phosphoric acid or acid phosphates from which phosphoric acid is partly volatilized upon evaporation. That this does not take place in the presence of a large excess of base, even from acid solutions, is shown positively by the experiments with magnesium nitrate.

#### INFLUENCE OF THE PRESENCE OF OTHER SALTS.

Ammonia salts in considerable quantities decrease slightly the intensity of the color reaction. Ammonium nitrate added to the unknown solution at the rate of 0.04 gram per 50 cc. gave readings on 4 parts per million of standard of only 3 parts, which increased a little on standing, but the solution soon precipitated.

<sup>1</sup> Subsequent work has confirmed these results in every instance.

<sup>2</sup> It seems possible that this apparent loss may be due to the formation of pyrophosphoric acid.—EDDTON.

Ammonium chloride does not give a water-white solution always—has a tendency to be slightly opaque, and it also prevents the full development of the color. The figures obtained are given in the table.

TABLE III.—EFFECT OF AMMONIUM SALTS.

Parts per million $\text{NH}_4\text{NO}_3$ .	Parts per million $\text{P}_2\text{O}_5$ added to $\text{NH}_4\text{NO}_3$ solution.	$\left\{ \begin{array}{c} - \\ \end{array} \right\}$	Parts per million $\text{P}_2\text{O}_5$ without $\text{NH}_4\text{NO}_3$ .	Solution with $\text{NH}_4\text{NO}_3$ commenced to precipitate.
4000	1.0	=	0.7	not in 5 min.
4000	4.0	=	2.0	nearly as dark but precipitated too rapidly to be sure.
4000	4.0	=	3.0	nearly as dark but precipitated too rapidly to be sure.
800	4.0	=	3.3	precipitated in 50 min.
800	4.0	=	3.7	" " 75 "

Calcium nitrate, barium chloride, potassium nitrate, and aluminum sulphate, separately and together, were added to solutions at the rate of 0.25 gram of each salt to 50 cc. of solution. None of these except the aluminum sulphate affected the readings more than 0.1 part per million, or within the limit of error of readings. Aluminum sulphate in this quantity gave a dark, opaque solution which could not be matched satisfactorily against the standard.

It was found that iron salts in considerable quantities exerted a marked influence not only on the color of the solution itself, in the first instance, an influence which it was found could be corrected for by reading against the standard, but there is also a reaction between the iron salt and the molybdate, a reaction which appears to bear a relation to the amount of iron present, and which possibly may be used for the estimation of the iron in solution. As iron is present in many soil extracts, the reaction of iron with the molybdate solution required careful study in order to determine the amounts and conditions which would vitiate the phosphate readings. The results of the investigation of this point are given in Table IV. Unless otherwise stated, the two solutions were identical in all particulars except that one contained iron in the amounts given in the table. The iron salt was made from pure wire, the solution of which was evaporated to dryness several times to remove traces of silica and hydrochloric acid.

TABLE IV.—COLOR PRODUCED BY IRON SALTS WITH MOLYBDATE SOLUTION.

*Preliminary Series.*

Parts per million of Fe in solution.	Parts per million $P_2O_5$ to equal color of Fe solution before molybdate was added.	Parts per million $P_2O_5$ to equal color of Fe solution after molybdate was added to Fe solution.	Parts per million of $P_2O_5$ to equal color produced by adding 1 part per million $P_2O_5$ to Fe solution containing molybdate.
4000	3.0	6.5	...
2000	..	3.0	...
2000	0.6	2.5	...
2000	..	4.0	1.05
2000	..	3.1	0.95
2000	..	3.0	1.10
400	2.2	3.2	...
200	0.8	1.6	1.10
80	0.2	0.8	1.00
40	0.1	0.3	1.00
40	0.1	0.5	...
40	0.1	0.5	1.00

*Final Series.*

100	0.1	{ 0.75 0.75 0.80
50	0.0	{ 0.40 0.40 0.50
20	0.0	{ 0.10 0.10
10	0.0	{ 0.00 0.00
8	0.0	{ 0.00 0.00
4	0.0	{ 0.00 0.00
2	0.0	{ 0.00 0.00

The presence of less than 20 parts of iron (Fe) per million of solution introduces no appreciable error in the determination, while as much as 50 parts per million vitiate the phosphate results, unless the amount of iron present is known and its reading subtracted from the total reading. As soil extracts seldom contain more than 0.1 to 5 parts per million of iron, further study of the influence of iron has been temporarily discontinued, but it is hoped to devote more attention to this point later. It is of course necessary, where the presence of considerable iron is indicated, to assure one's self that not more than 20 parts per million are present

before the reading can be accepted as representing phosphoric acid alone. This is quite readily ascertained by adding potassium sulphocyanide or ferrocyanide to the acidulated extract and matching the developed color against an iron standard.<sup>1</sup>

EFFECT OF VARYING THE AMOUNT OF NITRIC ACID PRESENT.

Woodman and Cayvan<sup>2</sup> found that the depth of color and the rapidity with which it developed depended to a certain extent on the amount of reagents present in the solution, and further state that the best results were obtained with 4 cc. of ammonium molybdate solution (50 grams of the salt per liter) and 2 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of the solution to be examined.

It appeared advisable to make an experimental study of these points in order to obtain data on the allowable variations in amounts of added reagents. To this end solutions containing different amounts of nitric acid and also different amounts of standard phosphate solution were compared with solutions containing 2 cc. of nitric acid and 4 cc. of molybdate. The results follow:

TABLE V.—EFFECT OF VARYING THE QUANTITY OF NITRIC ACID ADDED.

HNO <sub>3</sub> +	Na <sub>2</sub> HPO <sub>4</sub> +	Molybdate	=	Na <sub>2</sub> HPO <sub>4</sub> +	HNO <sub>3</sub> +	Molybdate.
Cc.	Cc.	Cc.		Cc.	Cc.	Cc.
1	1	4		0.83	2	4
2	1	4		1.04	2	4
3	1	4		1.10	2	4
4	1	4		1.15	2	4
5	1	4		1.24	2	4
6	1	4		0.98	2	4
7	1	4		0.97	2	4
8	1	4		0.88	2	4
10	1	4		0.84	2	4

The intensity of the color is sharply and regularly affected by the amount of nitric acid present, and it is of particular interest to note that there is a maximum point at which the color is most intense: with less acid or with more acid present the intensity of color is considerably reduced and it is evident that to obtain strictly comparable results the standard and the solution to be read must contain, in a given volume, sensibly the same amount of acid.

Possibly these results are also of interest in throwing light on the precipitation of ammonium phosphomolybdate and may ex-

<sup>1</sup> Sutton's "Volumetric Analysis," eighth edition, p. 245.

<sup>2</sup> *Loc. cit.*

plain the results sometimes obtained. It is a well-known fact that the color of the precipitate varies with the amount of acid present from a light lemon-yellow to a deep orange, and the speed with which the precipitate is formed also varies with the amount of nitric acid present. Under the best conditions this precipitation takes place rapidly and is complete; the supernatant fluid is practically as colorless as water, even when it contains a considerable amount of iron salt. On the other hand, under some other condition the precipitate forms slowly, is "muddy," filters and washes slowly, and shows a decided tendency to run through the filter, while the filtrate generally has a decided color, due apparently to the ammonium phosphomolybdate still in solution.

The above results show that the presence of 5 cc. of nitric acid (sp. gr. 1.07) per 50 cc. of solution gives the most intense color, and this amount has been adopted for this work. Whether or not this relation gives the optimum condition for the precipitation of ammonium phosphomolybdate, remains to be investigated.

#### EFFECT OF VARYING THE QUANTITY OF MOLYBDATE.

The effect of varying the quantity of molybdate was studied in the same way. The standard and the solution to be read were identical in all particulars except that in the standard the amount of molybdate present in 50 cc. was always 4 cc., while in the other solution the amount of molybdate varied.

TABLE VI.—EFFECT OF VARYING THE QUANTITY OF MOLYBDATE ADDED.

Molybdate Cc.	+ Na <sub>2</sub> HPO <sub>4</sub> Cc.	+ HNO <sub>3</sub> Cc.	=	Na <sub>2</sub> HPO <sub>4</sub> Cc.	+ molybdate Cc.	+ HNO <sub>3</sub> Cc.
2	1	5		0.85	4	5
4	1	5		1.00	4	5
6	1	5		1.15	4	5
8	1	5		0.97	4	5
12	1	5		0.96	4	5

The results show considerable differences due to varying the amount of molybdate. These differences are not as great nor is the maximum point as well defined as with different amounts of nitric acid, and there seems to be no reason for changing the amount of molybdate adopted by Woodman and Cayvan as giving the most satisfactory results.

From the foregoing results it appears reasonably certain that in order to obtain reliable and comparable results the standard and the unknown solution must always contain the same quantities of nitric acid and of molybdate and be at the same temperature.

Should different workers use different amounts of reagent, their results could not be strictly comparable.

#### EFFECT OF FILTER-PAPER.

In the experiments on the removal of silica and also in some of those on the loss of phosphoric acid on evaporation of the solution, it was observed that the readings were higher than they should have been. As all the work was done in platinum dishes the only point where other material could get in was where the solutions were filtered to remove silica. In order to determine if anything is taken up from the filter, solutions of various strength were passed through 7 cm. S. & S. No. 590 paper with the following results:

Parts per million before filtering.	Parts per million after filtering.	Gain, parts per million.
1	1.16	0.16
1	1.14	0.14
2	2.12	0.12
2	2.17	0.17
5	5.01	0.01
5.5	5.50	0.00

The filters were washed until filtrates had a volume of 50 cc. each. The results indicate that in passing through the filter these nitric acid solutions of phosphates have taken up silica, phosphoric acid or organic matter equal to an average reading of 0.15 part per million in four cases, while in two experiments there is no apparent gain. It seems probable that in these latter cases the amount taken up from the paper, is masked by incomplete removal of the phosphoric acid from the paper, in the volume of wash-water used. Beyond a doubt filtration introduces a plus error, which may only be apparent in very dilute solutions. Results given in this paper have been corrected in accordance with the above data.

#### REMOVAL OF SILICA.

As it is necessary to remove silica from the solution before reading, it was thought that this might be most expeditiously and certainly accomplished by treatment with hydrofluoric acid.

Repeated trials, however, showed that this is not true. While the silica was completely removed finally, it was found that it was necessary to remove all hydrofluoric acid before standardizing, as the smallest quantity of fluorides prevented completely the develop-



ment of the color. As at least three evaporations with nitric acid were required to accomplish the removal of hydrofluoric acid, the standard procedure of evaporation with nitric acid and drying at  $100^{\circ}$  for two hours was returned to.

The writer's experience confirms the statement of Woodman and Cayvan that a single evaporation removes completely the silica from the solution in those cases where lime and magnesia salts are absent, but where lime and magnesia salts are present in considerable quantities, the amount of silica remaining in solution after one evaporation and filtration is too great to be neglected.

For the study of these points a solution of sodium silicate was prepared which, by gravimetric analysis, gave from first evaporation and filtration, 266 parts per million  $\text{SiO}_2$ ; second evaporation and filtration, 2 parts per million  $\text{SiO}_2$ ; third evaporation and filtration, 0 part per million  $\text{SiO}_2$ ; total, 268 parts per million  $\text{SiO}_2$ .

The filtrate from the third evaporation contained no silica by the colorimetric method. 250 cc. of this silicate solution were transferred and made up to 1 liter, with the view of obtaining a solution containing about as much dissolved silica as is found in many soil extracts.

By calculation from the above determinations this contained 67 parts  $\text{SiO}_2$  per million; first evaporation and filtration removed 63 parts  $\text{SiO}_2$  per million; second evaporation and filtration removed 2 parts  $\text{SiO}_2$  per million; total recovered, 65 parts  $\text{SiO}_2$  per million.

By the colorimetric method the solution contained 65 parts  $\text{SiO}_2$  per million.

The filtrate from the first evaporation contained, colorimetrically, less than 0.05 part per million, average of four determinations. The filtrate from the second evaporation contained, colorimetrically, less than 0.1 part per million. The filtrate from the third evaporation contained, colorimetrically, less than 0.1 part per million.

In order to determine the effect of the presence of lime and magnesia salts, a solution containing 25 mg. of calcium nitrate and 25 mg. of magnesia was added to portions of silicate solution and silica determined colorimetrically as well as gravimetrically.

Gravimetrically obtained: First evaporation and filtration re-

moved 63 parts  $\text{SiO}_2$  per million; second evaporation and filtration removed 5 parts  $\text{SiO}_2$  per million; total, 68.

Colorimetrically obtained: 67 parts  $\text{SiO}_2$  per million; calculated, 67 parts  $\text{SiO}_2$  per million.

Filtrate from the first evaporation gave, colorimetrically, 1.42 parts  $\text{SiO}_2$  per million. Filtrate from the second evaporation gave, colorimetrically, 0.1 part  $\text{SiO}_2$  per million. Filtrate from the third evaporation gave, colorimetrically, less than 0.1 part  $\text{SiO}_2$  per million.

From these results it appears that in the absence of lime and magnesia salts the silica left in most soil solutions after one evaporation may be neglected, but in the presence of these salts two evaporations are necessary.

#### THE COLORIMETRIC DETERMINATION OF SILICA.

In their study of the effect of silica on the development of color, Woodman and Cayvan<sup>1</sup> found that while some color was developed instantly, it did not reach the maximum intensity in less than from one and one-half to two and one-half hours, and their results further show that the color due to the formation of the ammonium silico-molybdate is about one-tenth that produced by an equivalent amount of ammonium phosphomolybdate. This reaction apparently was used first by Jolles and Neurath<sup>2</sup> for the determination of silica in waters. For our determination of silica a solution of sodium silicate was prepared and the silica determined gravimetrically. Portions of this solution were compared with the standard phosphate solution under identical conditions as to temperature, nitric acid, molybdate solution, and volume. The data obtained are given in the following table:

TABLE VII.—READINGS OF  $\text{SiO}_2$  IN TERMS OF  $\text{P}_2\text{O}_5$ .

<i>Preliminary Series.</i>		
Mg. $\text{SiO}_2$ in solution read.	Mg. $\text{P}_2\text{O}_5$ required to equal color produced by $\text{SiO}_2$ .	1 mg. $\text{SiO}_2$ equals mg. $\text{P}_2\text{O}_5$ .
0.10	0.19	1.90
0.10	0.175	1.75
0.20	0.35	1.75
0.20	0.37	1.85
0.30	0.51	1.70
0.30	0.57	1.90

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ztschr. angew. Chem.* (1898), p. 315.

TABLE VII—(Continued).

Mg. $\text{SiO}_2$ in solution read.	Mg. $\text{P}_2\text{O}_5$ required to equal color produced by $\text{SiO}_2$ .	1 mg. $\text{SiO}_2$ equals mg. $\text{P}_2\text{O}_5$ .
0.50	0.92	1.84
0.51	0.90	1.78
0.70	1.35	1.93
0.70	1.28	1.83
1.00	1.80	1.80

Average, 1.82

*Final Series.*

0.068	0.1265	1.86
0.136	0.2464	1.81
0.204	0.3741	1.83
0.272	0.4785	1.78
0.340	0.5907	1.73

Average, 1.80

The table shows that the intensity of color produced by the silica is on an average 1.8 times that produced by an equivalent amount of phosphoric acid. That is, the phosphate readings divided by 1.8 or multiplied by 0.55 equals  $\text{SiO}_2$ .<sup>1</sup> It will be seen from the final results, in which most reliance is placed—as they were obtained after considerable experience with the method—that there is a gradual decrease in this factor with increasing quantities of silica. The time required for the full development of the color was much shorter than found by Woodman and Cayvan, apparently reaching the maximum in less than twenty minutes, after which time it remained stationary for some time and then slowly faded.

On the basis of this work the procedure which I have adopted for the determination of silica and phosphoric acid in soil solutions is as follows:

The water or extract is tested for iron by adding potassium ferrocyanide to the acidified solution. The absence of interfering amounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a Chamberland filter (reject the first 100 cc. that passes) or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or color is corrected for by determining its amount in terms of the

<sup>1</sup> These results differ greatly from those given by Woodman and Cayvan, but so far no time has been available for further study of this point.

standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract 5 cc. of nitric acid (sp. gr. 1.07) and 4 cc. of molybdate solution. Place in the camera, allow ten to thirty minutes for development of color and compare with a standard phosphate solution, which may conveniently contain 10 parts per million of phosphorus pentoxide and be contained in a sliding tube connected by rubber tubing with a side neck tube graduated in cubic centimeters within the camera. (The color of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh each day.) The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 cc., equals  $P_2O_5 + SiO_2$  in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice with a filtration between the evaporations in a porcelain or platinum dish with 3 cc. nitric acid (sp. gr. 1.07) plus a little magnesium nitrate,<sup>1</sup> heated two hours in a water oven, 5 cc. nitric acid (sp. gr. 1.07) added, filtered, washed to about 45 cc., placed in a camera and compared. If colored, the reading is noted, and is finally subtracted from the total reading. Add 4 cc. of ammonium molybdate and thoroughly mix. Place in the camera and compare after two to five minutes. The corrected reading calculated to volume of 100 cc. is  $P_2O_5$  in parts per million of solution. This reading subtracted from the  $SiO_2 + P_2O_5$  reading and the difference multiplied by 0.55 gives the silica.

Where the original solution is too much colored with organic matter to be accurately corrected for by reading the color thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gram magnesium nitrate<sup>1</sup> and burn off the organic matter, take up with water + 3 nitric acid, evaporate to dryness and heat two hours in the water oven. Add 5 cc. nitric acid and proceed as above. Readings =  $P_2O_5$ . In this case silica is not determined.<sup>2</sup>

The results given in the following table have been obtained in the course of the work.

<sup>1</sup> In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

<sup>2</sup> Or the organic matter may be destroyed by treating with aqua regia in the presence of sufficient base to prevent loss of phosphoric acid.

TABLE VIII.—DETERMINATION OF  $\text{SiO}_2$  +  $\text{P}_2\text{O}_5$  IN MISCELLANEOUS SAMPLES.

	$\text{SiO}_2$ present.	$\text{SiO}_2$ found.	$\text{P}_2\text{O}_5$ present.	$\text{P}_2\text{O}_5$ found.
	Parts per million.		Parts per million.	
Sodium phosphate solution, No. 1.....	....	....	49.6	48.5
“ “ “ “ 2.....	....	....	99.1	101.4
Sodium silicate solution .....	182.0	180.5	...	....
Soil extract, No. 13 .....	....	24.4	....	2.0
“ “ “ 14 .....	....	23.4	....	2.95
“ “ “ 15 .....	....	21.2	....	2.95
“ “ “ 16 .....	....	19.1	....	2.95
“ “ 1st foot.....	....	17.9	....	7.3
“ “ 2nd “ .....	....	8.2	....	1.0
“ “ 3rd “ .....	....	7.8	....	3.1
“ “ 4th “ .....	....	11.9	....	1.4
“ No. 2806, sandy truck soil .....	....	2.0	....	10.0
“ “ 2795, loam soil .....	....	38.0	....	8.0
“ “ 3, clay soil .....	....	30.0	....	8.0
“ “ 2804, “ “ .....	....	28.0	3 grav.	4.0
Sodium phosphate solution, original solution <sup>1</sup> .....				73.1
“ “ “ first 50 cc. through Chamberland filter .				59.1
“ “ “ second 50 cc. “ “ “ ..				67.6
“ “ “ third 50 “ “ “ ..				71.8
“ “ “ left in 50 “ in “ “ ..				80.3
“ “ “ rinsings of “ “ ..				80.3
“ “ “ original solution .....				80.25
“ “ “ first 50 cc. through Chamberland filter				54.9
“ “ “ second 50 cc. “ “ “				71.8
“ “ “ third 50 “ “ “				84.5
“ “ “ left in 50 “ in “ “				97.2
“ “ “ rinsings of “ “				84.5

In pure solutions the method gives very close readings and very accurate results on dilute solutions. The average error has been well within 0.2 part per million of the solution read where these solutions did not contain more than 10 parts per million and the readings fall below 60 scale divisions on the colorimeter tube. This insignificant error of reading may give rise to larger differences when calculated on the basis of the dry soil. Should the solution to be examined contain more than 10 parts per million, its dilution to this strength and subsequent calculation to the basis of the original solution or to the dry soil may so multiply this error of reading as to render the results valueless. This has been a serious handicap to the method. The use of more concentrated solutions

<sup>1</sup> Readings made for Professor F. K. King.

is obviously the rational way out of the difficulty. It is also obvious that here we are limited to the use of concentrations from which the phosphomolybdate will not precipitate, within an hour or so. As solutions of greater concentration than 10 parts per million cannot be read closely in 25 mm. tubes, with ordinary light, and as larger tubes were not available, I have not tried greater concentrations in larger tubes, but in several experiments using a strong standard (between 50 and 100 parts per million), in shallow depths in the 25 mm. tubes, it was not found possible to read closer than from 0.5 to 1 part per million. This error of reading, when calculated back to the original solution or to the dry soils, gives as great an error as the closer readings of the more dilute solutions, so this line of study was not carried farther.

In addition to this study conducted with known solutions, the method has also been applied to the soil samples sent out this year by the Association of Official Agricultural Chemists. The results thus obtained are given in the following table, with results obtained by the standard methods for determining phosphoric acid. The average total reading in scale divisions and the corrections on each sample, also in scale divisions, are given in the table. These corrections are for original color of the liquid and for filter paper.

TABLE IX.—PHOSPHORIC ACID SOLUBLE IN DISTILLED WATER. PARTS PER MILLION OF DRY SOIL. 400 CC. OF SOLUTION USED FOR THE DETERMINATIONS.

No.	Average total scale readings.	Correction in scale readings.	Reading due to $P_2O_5$ .	$P_2O_5$ colorimetric.	$P_2O_5$ volumetric.
2	13.5	1.5	12.0	1.50	1.33
3	10.0	1.5	8.5	1.06	0.64
4	10.0	1.5	7.5	0.94	1.26
5	10.0	3.0	7.0	0.87	0.99
6	48.5	5.5	42.0	5.60	5.10
7	23.0	2.5	20.5	2.56	2.63
8	20.0	3.0	17.0	2.12	1.95

The results given are all that the writer has obtained on soils. No determinations have been rejected.

#### PRECAUTIONS.

The method is so delicate (one scale division means one-half of one part per million on basis of dry soil when the solution is prepared by treating 1 part of soil with 5 parts of water and taking 50 cc. for the determination), and as has been shown there

are so many points at which errors may be introduced, that a final word as to the precautions to be observed in handling it may be given with propriety.

The sodium phosphate ( $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ ) from which the standard is made must be practically pure, and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxide per liter, and then dilute this to 10 parts per liter for the reading standard. The greatest care should be used in making this standard as it is here where errors count. Ten cc. of the 100 parts per liter solution should be run into a standardized 100 cc. flask from an accurately graduated burette. Make up to volume at  $20^\circ\text{--}25^\circ\text{C.}$  with distilled water (free from  $\text{SiO}_2 + \text{P}_2\text{O}_5$ ), add 10 cc. of nitric acid (1.07) and 8 cc. of ammonium molybdate and mix thoroughly. This is the standard with which the unknown solutions are to be compared and it should be made fresh each day.

All reagents including distilled water must be kept in Jena glassware, tested from time to time and made fresh when a mixture of them shows color after standing some time.

As the colorimetric tubes may have a slight color themselves, each should be tested and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a 1 part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron (Fe).

A correction must be established for each package of filter-paper used. This correction is small, but not to be neglected on S. & S. No. 590 paper.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

Observing all precautions and making all corrections there is a maximum error of  $\pm 2$  scale divisions (each scale division = 1 cc.) in the reading. When the soil solution is made by treating 1 part of soil with 5 parts of water and 50 cc. are taken for the determination, the error on the dry soil is  $\pm 2$  parts per million ;

when 100 cc. are taken for the determination the error is  $\pm 1$  part per million, so that the working errors may only be neglected when at least 200 cc. of solution are taken for the determination.

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## A RAPID METHOD FOR DETERMINING SULPHUR IN COAL AND COKE.

BY CARL SUNDSTROM.

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THE necessity for a rapid method of determining sulphur in fuels, led to the investigation of the action of sodium peroxide on coal. This reaction was suggested by Professor S. W. Parr's paper on his calorimeter as given in this Journal, 22, 646.

It was found that coal and coke, ignited with a liberal excess of the peroxide, left almost no residue insoluble in a faintly acid solution, and it became a question only of a suitable apparatus. Apparatus was required that would be cheap, in which the charge could be easily ignited, and out of which the melt could be quickly dissolved. For coke, a covered nickel crucible of about 30 cc. capacity answered every purpose; but coal had to be confined in a bomb, as it always burned with explosive violence.

### ANALYSIS OF COKE.

700 milligrams of finely powdered coke are intimately mixed with 13 grams of sodium peroxide, in a nickel crucible of about 30 cc. capacity. The peroxide must be finely powdered and dry, and should be weighed rapidly and brushed off the watch-glass with a glass brush. The crucible is covered and a 3-inch fuse is inserted under the edge of the cover and extended well into the mixture. The crucible is then supported on a triangle and placed in about  $\frac{3}{4}$  inch of water; the fuse is ignited, and in three or four minutes, when the mass has cooled sufficiently, the crucible and cover are placed in a small beaker and 30 cc. water added. The mass dissolves completely in about two minutes. After rinsing off the crucible and cover, the solution is made just acid with hydrochloric acid, and filtered through a small filter. The filtrate is boiled and precipitated with barium chloride in the usual way.

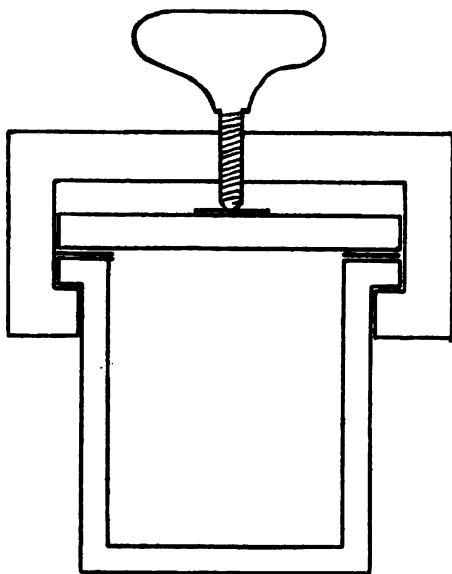
The fuses are made by nitrating cotton wicking with a mixture of 1 part fuming nitric acid (sp. gr. 1.50) and 2 parts concentrated



sulphuric acid (sp. gr. 1.84) for twelve hours, at 15° C. The nitrated cotton is then washed in running water for twelve hours, to remove every trace of acid, and dried at laboratory temperature. When dry, it is treated with a cold, nearly saturated solution of potassium nitrate for an hour; then the excess of solution is pressed out, dried as before, and finally cut into lengths of 3 inches ready for use.

#### ANALYSIS OF COAL.

The apparatus consists of a small, cylindrical, steel bomb, of the following dimensions: 1¼ inch internal diameter, 1½ inch internal depth, sides and bottom ⅛ inch thick, and a ⅙ inch flange



Sketch of bomb—full size.

around the top. A cover plate  $\frac{3}{16}$  inch thick and 1¾ inch in diameter, is clamped on by means of a small clamp, fitting under the bomb flange and pressing down the cover with one central screw. The bottom is hemispherical inside. The cover is insulated from the bomb by a thin mica gasket, and from the screw of the clamp by a piece of ordinary red fiber.

700 milligrams of finely powdered coal are mixed with 13 grams of sodium peroxide in the bomb, and compressed by means of a small press or vice. A No. 36 iron wire, 4 inches long, is now

inserted, one end under the mica gasket and touching the bomb, the other end above the gasket and in contact with the cover, the wire being looped so as to touch the mixture in the bomb. A current of 4 amperes is used to fuse the wire, one terminal in contact with the bomb, the other applied to the cover. After a minute or two, cool the bomb in a little water, unscrew the clamp and dissolve the mass, treating exactly as in the coke analysis.

This method compares very well with Eschka's method and requires much less time and cheaper apparatus while there is less liability of contamination with impure chemicals and exposure to gas flames. The peroxide used seldom contained any sulphates.

The following are some of the results obtained:

	Per cent. sulphur by Eschka's method.	Per cent. sulphur by peroxide method.
Coal and coke.		
River View coal .....	1.69	1.64
" " " .....	1.59	1.57
Hocking Valley, pea .....	1.95	1.96
" " slack .....	1.690	1.694
Coke (mixture) .....	1.26	1.21
Pittsburg coke .....	0.89	0.88
Connellsville coke .....	1.67	1.73
Coke mixture .....	2.027	2.031

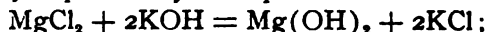
DETROIT, October 18, 1902.

## A STUDY OF MAGNESIUM AND MANGANOUS HYDROXIDES AND OF BARIUM SULPHATE WITH RESPECT TO THE PHENOMENA OF ADHESION AND OF SOLUTION.

BY HARRISON EASTMAN PATTEN.

Received November 27, 1902.

THE work on aluminum,<sup>1</sup> iron,<sup>2</sup> zinc,<sup>3</sup> and chromium<sup>4</sup> has shown that the action of their hydroxides in carrying down other substances into precipitation is chemical, and under certain conditions not proportional to the mass of precipitate. I have examined the action usually expressed by the equation



also

<sup>1</sup> "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydroxide," *Am. Chem. J.*, 8, 23.

<sup>2</sup> "A Study of Ferric Hydroxide in Precipitation," *Ibid.*, 10, 512.

<sup>3</sup> Unpublished.

<sup>4</sup> "Chromic Hydroxide in Precipitation," *Ibid.*, 18, 608; also "Recherches sur le sulfate chromique, ses transformations et les acides complexes qui en derivent," *Ann. chim. phys.*, 7, 4 (1895).

$\text{MgCl}_2 + 2\text{KOH} + \text{K}_2\text{SO}_4 = \text{Mg}(\text{OH})_2 + 2\text{KCl} + \text{K}_2\text{SO}_4$   
to ascertain whether magnesium hydroxide acts in a similar manner.

## SOLUTIONS.

Solutions as described below were used in the work:

(1) For the magnesium solution, 20.2963 grams of crystallized magnesium chloride was made up to 1 liter at 20°. This solution contained 0.0070 gram chlorine, and 0.00308 gram magnesium oxide per cubic centimeter.

(2) A dilute solution of potassium hydroxide, standardized by oxalic acid and gravimetrically. It contained 0.0261 gram potassium hydroxide per cubic centimeter.

(3) A dilute solution of sulphuric acid, standardized against the potassium hydroxide solution both volumetrically and gravimetrically (weighed as  $\text{K}_2\text{SO}_4$ ). It contained 0.04206 gram sulphuric acid per cubic centimeter.

As a preliminary step, the amount of potassium hydroxide required for exact precipitation of the magnesium in Solution (1) was determined.

## GENERAL METHOD.

The filtrates were analyzed and the percentage of each constituent found deducted from that of the total introduced. The difference gives the percentage of the constituent in the precipitate, which may not be analyzed directly, since washing or diluting the solution in which the precipitate is formed changes its composition. In the case of magnesium, the precipitated hydroxide is soluble in water.

A blank determination of the magnesium chloride was made: 50 cc. magnesium chloride stock solution was made up to 500 cc. at 20°, four portions were drawn off with a 50 cc. pipette and the magnesium oxide and chlorine determined in duplicate.

$$\text{MgO} \begin{cases} 0.0207 \text{ gram} \\ 0.0207 \text{ gram} \end{cases} \quad \text{Cl} \begin{cases} 0.0040 \text{ gram} \\ 0.0042 \text{ gram} \end{cases}$$

Experiments were now made with 44.24 cc. sulphuric acid, neutralized to potassium sulphate by the equivalent amount of potassium hydroxide, and 50 cc. stock solution of magnesium chloride as constant factors, the magnesium being precipitated by varying amounts of potassium hydroxide. The above constituents were

made up to 500 cc. at 20°, allowed to stand twenty minutes, well shaken and four portions of mixed precipitate and solution drawn off with a dry 50 cc. pipette and labeled "totals". The solution and precipitate remaining was thrown upon a dry filter-paper, the clear filtrate brought back to 20°, and five portions drawn off with a 50 cc. pipette and labeled "filtrates".

The "totals" for magnesium oxide were redissolved by hydrochloric acid in some excess, ammonia added to alkaline reaction and the magnesium precipitated cold as magnesium ammonium phosphate, and weighed as pyrophosphate.

The "totals" for chlorine were redissolved by nitric acid, precipitated hot with silver nitrate solution, and the magnesium removed by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter. The chlorine was then weighed as silver chloride.

The "filtrates" for magnesium oxide and chlorine were analyzed in the same manner as the "totals". As in the work with aluminum, chromium, iron and zinc, it was assumed that re-solution by hydrochloric or nitric acid would liberate any constituents carried down in the precipitation with potassium hydroxide.

It was considered unnecessary to determine the potassium oxide in the "totals" and "filtrates," for two reasons: first, because in all the foregoing work in this line no carrying down of potassium was observed short of re-solution in the alkali; second, the negative results of the work on magnesium oxide, chlorine and sulphur trioxide in this investigation indicate the absence of such action.

No good method of separating the magnesium oxide from the sulphur trioxide in "totals" and "filtrates" being available, two different methods were used to ascertain whether the sulphur trioxide enters into the reaction.

(1) The amount of magnesium oxide precipitated in presence of *potassium sulphate* by a definite amount of potassium hydroxide, should be greater than the amount precipitated in absence of the sulphate—if *sulphur trioxide enters into the reaction*.<sup>1</sup>

(2) Magnesium oxide or chloride should be carried down into precipitation by barium sulphate. The four elements already mentioned show this reciprocal action, as does also manganese, of which I shall speak later.

<sup>1</sup> Series II., "Chromic Hydroxide in Precipitation," *loc. cit.*; "A Study of Ferric Hydroxide in Precipitation," *loc. cit.*

TABLE I.

Experiment.	KOH.	"Total" MgO.	"Filtrate" MgO.	"Precipitate" MgO.	"Total" Cl.	"Filtrate" Cl.	"Precipitate" Cl.	"Precipitate" % MgO.
I	2	0.02065 0.02071	only a trace	0.0207	0.0036 0.0035	0.0037 0.0040	0.0000	100.00
II	6 (2) 300 cc. MgCl <sub>2</sub>	0.1190+ 0.1190—	0.0026 0.0020	0.1167	0.2082 0.2085	0.2086 0.2088	0.0000	98.06
III	6 (1½) 300 cc. MgCl <sub>2</sub>	0.1174 0.1180	0.0281 0.0276	0.0899	0.2080 0.2085	0.2081 0.2087	0.0000	76.38
New solution IV	1½ + K <sub>2</sub> SO <sub>4</sub>	0.1926 0.1927	0.0480 0.04807	0.1446	0.3445 0.3443	0.3442 0.3438	0.0004	75.07
V	1½	0.1928 0.1931	0.0484 0.0481	0.1447	0.3431 0.3432	0.3427 0.3429	0.0003	75.07
VI	1 + K <sub>2</sub> SO <sub>4</sub>	0.1936 0.1942	0.0958 0.0963	0.0979	0.3430 0.3425	0.3433 0.3429	0.0000	50.46
VII	1	0.1941 0.1940	0.0968 0.0966	0.0974	0.3426 0.3429	0.3427 0.3426	0.0001	50.46

*Experiment I.*—The system was made up according to the equation  $\text{MgCl}_2 + 2\text{KOH} = \text{Mg}(\text{OH})_2 + 2\text{KCl}$ , using 50 cc. of magnesium chloride solution to 22.2 cc. potassium hydroxide solution. No potassium sulphate was introduced here since the object was to determine if chlorine were carried down into precipitation by the magnesium hydroxide. No chlorine was found in the precipitate (see Table I, Exp. I). A trace of magnesium was obtained in the filtrate by further addition of potassium hydroxide, showing that magnesium chloride is not completely precipitated by 2 molecules of potassium hydroxide. As the mass of precipitate was so small, for this concentration, and as "adhesion" in the cases of chromium, iron, aluminum and zinc hydroxides is more marked in concentrated solutions, the next two experiments were made up each with six 50 cc. portions of magnesium chloride solution instead of one 50 cc. portion as in this experiment.

*Experiment II.*—The system was made up according to the equation  $\text{MgCl}_2 + 2\text{KOH} = \text{Mg}(\text{OH})_2 + 2\text{KCl}$  (see Table I, Exp. II., for results). This shows no chlorine carried down into precipitation. Since adhesion is more marked at incomplete precipitation than at complete precipitation, in the next experiment I used  $1\frac{1}{2}$  KOH.

*Experiment III.*—The system was made up according to the equation  $\text{MgCl}_2 + 1\frac{1}{2}\text{KOH} = ?$  (see Table I, Exp. III, for results). Here again no chlorine is carried down by the precipitate.

The stock supply of magnesium chloride being now exhausted, a new solution (4) was made up: 203 grams  $\text{MgCl}_2 + 6\text{H}_2\text{O}$  were dissolved in water and diluted to 1000 cc. of solution at  $20^\circ$  C. One 50 cc. portion was drawn off and made up to 500 cc. at  $20^\circ$  C. Of this solution each 50 cc. contained:

$$\begin{array}{ll} \text{MgO} \left\{ \begin{array}{l} 0.1926 \text{ gram} \\ 0.1925 \text{ gram} \end{array} \right. & \text{Cl} \left\{ \begin{array}{l} 0.3445 \text{ gram} \\ 0.3440 \text{ gram} \end{array} \right. \end{array}$$

For 50 cc. of stock solution of magnesium chloride (4), 212.5 cc. potassium hydroxide were required to precipitate completely the magnesium. The calculated amount of potassium hydroxide was 207 cc.

Now the attempt was made to ascertain if sulphur trioxide is carried down into precipitation. As was stated in "General

Method," no good means of separation being at hand a difference method was resorted to. The work on chromium and iron showed that in a partially precipitated system (which had been filtered or allowed to settle) further precipitation was caused by the addition of a little sulphate solution, and in some cases<sup>1</sup> no definite precipitate was obtained unless some soluble sulphate was present. From this influence of sulphur trioxide on the amount of hydroxide formed at fractional precipitation, I assume that if sulphur trioxide is carried down into precipitation by magnesium hydroxide, the amount of magnesium hydroxide precipitated by, say, 1.5 molecules of potassium hydroxide will be greater in the presence of sulphur trioxide than in its absence. If then, the amount of magnesium hydroxide precipitated by 1.5 molecules of potassium hydroxide is the same with and without sulphur trioxide present, I conclude that no adhesion takes place.

For results see Experiments IV, V, VI, VII, Table I, and the accompanying plate, curve 6.

The same amount of magnesia is precipitated in Experiment IV with potassium sulphate present as in Experiment V with potassium sulphate absent; likewise in Experiments VI and VII. Since no sulphur trioxide is carried down into precipitation at these fractional points it was considered unnecessary to try an experiment at complete precipitation, inasmuch as the other elements worked with show their greatest "adhesion" activity at these points. Further, since magnesium gives a definite precipitate at the fractional points in absence of sulphur trioxide, it ought to carry down chlorine into precipitation if it exercises the property of "adhesion"; Experiments I, II, and III show no chlorine carried down.

*Experiment VIII.*—It was determined that magnesium hydroxide precipitated from magnesium chloride by potassium hydroxide in aqueous solution does not redissolve in excess of potassium hydroxide.

*Experiment IX.*—Twelve different barium sulphate determinations which had been made from solutions containing magnesium chloride, potassium sulphate and hydrochloric acid by addition of barium chloride were treated as follows: fused with sodium carbonate, the alkali washed out with water, the insoluble barium

<sup>1</sup> Fractional precipitation of chromium chloride by less than three molecules of potassium hydroxide. See "Chromic Hydroxide in Precipitation," *loc. cit.*

carbonate dissolved in hydrochloric acid, reprecipitated by ammonium carbonate to remove the barium, and the filtrate tested for magnesium by sodium hydrogen phosphate. Not a trace of magnesium was found.

#### DISCUSSION.

These results may be summarized thus: (1) Magnesium hydroxide does not carry down into precipitation with it either chlorine or sulphur trioxide. (2) Barium sulphate does not carry down into precipitation either magnesium oxide or chloride. (3) More than the theoretical amount of potassium hydroxide is required to completely precipitate magnesium hydroxide from a magnesium chloride solution in water at the concentration and temperature studied. On this last point more work should be done.

#### MANGANOUS HYDROXIDE.

*Method.*—The general method used in this investigation was the same as for chromium and iron. The sulphur trioxide was determined directly in "totals" and "filtrates" after the manganese had been removed. This removal was effected in the following manner: Sodium acetate solution was added to the "filtrates" and "totals" and the manganese precipitated as  $MnO_2$  by bromine, the excess of bromine boiled off and the  $MnO_2$  filtered off, well washed, and ignited and weighed as  $Mn_2O_4$ . The filtrate from this  $MnO_2$  was concentrated and the  $SO_3$  determined as  $BaSO_4$ . In the case of the "totals," re-solution of the manganous hydroxide was effected with hydrochloric acid just before the sodium acetate was run in. Occasionally the barium sulphate determinations showed a slight coloration, but the quantity of manganese present was of course negligible. I found this method efficient. Re-solution of these complex precipitates of chromium, iron, manganese, zinc, and aluminum, in hydrochloric or nitric acid has in every case proved sufficient to split them into determinable components.

The chlorine was determined in presence of manganese, a re-solution with nitric acid being first effected, and then all manganese was washed out of the silver chloride by a wash-water containing 25 cc. concentrated nitric acid and 0.1 gram silver nitrate per liter.

*Solutions.*—A. 98.9 grams  $MnCl_2 + 4H_2O$  was dissolved in water and made up to 500 cc. at 20° C. This solution was found



to contain the equivalent of 0.05186 gram  $\text{MnO}$  per cubic centimeter. *B.* A solution of potassium hydroxide containing 0.02705 gram  $\text{KOH}$  per cubic centimeter at  $20^\circ \text{C}$ . *C.* A solution of sulphuric acid containing 0.04046 gram per cubic centimeter at  $20^\circ \text{C}$ .

Experiments I, II, III, IV, V were made as shown in Table II. Each system contained 50 cc. manganous chloride, Solution *A*; 44.24 cc. sulphuric acid, Solution *C*, neutralized to potassium sulphate by 75.63 cc. of potassium hydroxide, Solution *B*; and varying amounts of potassium hydroxide to cause the precipitation. In every case the potassium sulphate was run into the flask; next the manganous chloride; and finally the potassium hydroxide. Then the system was made up to 500 cc. at  $20^\circ \text{C}$ . and well shaken, whereupon four 50 cc. portions were drawn out with a pipette and labeled "totals." The remaining precipitate and solution were thrown upon a dry filter-paper, the filtrate received in a dry flask, and brought back to  $20^\circ \text{C}$ . when four 50 cc. portions were drawn off, and labeled "filtrates." Throughout the investigation of chromium, manganese and magnesium, the same pipette was used.

#### DISCUSSION.

For results see Table II; also curves 7 and 8 in the plate. The chemical nature of adhesion is clearly shown here as well as in the case of iron, zinc, chromium and aluminum. Experiment I shows no sulphur trioxide in the precipitate, though the mass of precipitate is a maximum. Experiment II shows that 15.34 per cent. of the total sulphur trioxide is in the precipitate, while the mass of precipitate is some 9 per cent. less than in Experiment I. Experiment III shows 19.3 per cent. of the total sulphur trioxide in precipitation, while the mass of precipitate is still less than in Experiment II. Experiment IV confirms Experiment III, giving the maximum sulphur trioxide carried down. Experiment V shows a falling off in the sulphur trioxide in precipitation, but if we remember how small the amount of precipitated manganous hydroxide is at this point (0.5 molecule  $\text{KOH}$ ) the strength of the action is seen to be considerable.

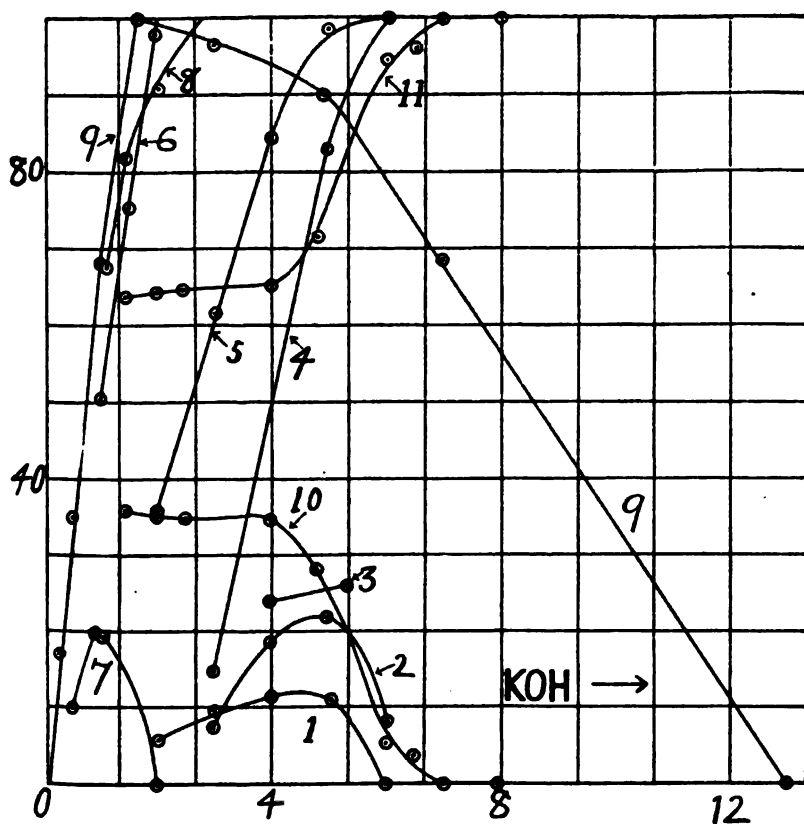
No chlorine was carried down at 1.5 or 1.1 molecules of  $\text{KOH}$ ; hence this "adhesion" is seen to be selective—the sulphur trioxide is taken, and the chlorine left.

TABLE II.

Exp.	KOH + $\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub>	MnO "total."	MnO "altine."	MnO "prec."	SO <sub>4</sub> "total."	SO <sub>4</sub> "fil."	SO <sub>4</sub> "prec."	Cl "total."	Cl "fil."	Cl "prec."	Total \$ SO <sub>4</sub> in "prec."	Total \$ MnO in "prec."
I	2	0.2593	0.0146	0.2347	0.1381	$\left. \begin{matrix} 0.1379 \\ 0.1368 \end{matrix} \right\}$	0.0000	.....	.....	.....	....	90.51
II	1 $\frac{1}{4}$	0.2593	0.04371	0.2122	0.1382	$\left. \begin{matrix} 0.1186 \\ 0.1134 \end{matrix} \right\}$	0.0212	0.3307	$\left. \begin{matrix} 0.3335 \\ 0.3321 \end{matrix} \right\}$	0.0000	15.34	81.83
III	1 $\frac{1}{16}$	0.2593	0.0833	0.1760	0.1376	$\left. \begin{matrix} 0.1110 \\ 0.1111 \end{matrix} \right\}$	0.0266	0.3298	$\left. \begin{matrix} 0.3302 \\ 0.3340 \end{matrix} \right\}$	0.0000	19.33	67.86
IV	1	0.2593	.....	.....	0.1384	$\left. \begin{matrix} 0.1103 \\ 0.1106 \end{matrix} \right\}$	0.0270	.....	.....	.....	19.50	....
V	$\frac{1}{4}$	0.2593	.....	.....	0.1378	$\left. \begin{matrix} 0.1244 \\ 0.1247 \end{matrix} \right\}$	0.0133	.....	.....	....	9.65	....

I think it probable that in absence of sulphur trioxide the chlorine would be carried down, since ferric hydroxide shows this same selective action and does carry down chlorine in absence of sulphur trioxide.

Since in the case of iron, potassium appears in the precipitate only at 8 molecules of potassium hydroxide, and in the case of chromium, potassium does not appear at all up to 8 molecules of



potassium hydroxide, it was considered unnecessary to determine potassium in the present investigation.

In the plate, I have plotted curves which show the per cent. of oxide and of sulphur trioxide in the precipitates obtained by adding various amounts of potassium hydroxide to the chloride. Ordinates are in per cent. of constituent; abscissas, in molecules of potassium hydroxide required to produce the precipitate. Curve

1 is the per cent. of total sulphur trioxide in the precipitate of ferric hydroxide; curve 2, the same for chromic hydroxide; curve 3, the same for ferric hydroxide (produced from a solution of ferric chloride having twice the concentration of that used for curve 1).<sup>1</sup> Curve 7 is the same for manganous hydroxide. Curve 4 gives the per cent. of total chromium trioxide precipitated by varying amounts of potassium hydroxide in presence of a fixed amount of potassium sulphate. Curve 5 is the same for ferric oxide. Curve 6, the same for magnesium oxide—presence or absence of potassium sulphate has no effect on the trend of the curve. Curve 8, the same for manganese oxide. Curve 9, the same for zinc oxide.<sup>2</sup> Curve 10 is the per cent. of total sulphur trioxide in the precipitate whose remaining constituent is aluminum trioxide, the per cent. of which is given in curve 11.<sup>3</sup>

My results as plotted in curve 7 show that the action of manganous hydroxide in carrying down sulphur trioxide into precipitation is truly chemical in nature, since the maximum carrying-down effect is observed far short of the maximum quantity of manganous hydroxide, as may be seen by reference to curve 8. The carrying down of chlorine and of potassium oxide remains to be investigated.<sup>4</sup> The results show, too, that the standard equations for the reaction between manganese chloride and potassium hydroxide, and between magnesium chloride and potassium hydroxide in aqueous solution do not represent the facts (see curves 6 and 8; likewise, 9 and 11). The distribution of the constituents of these systems is dependent upon temperature, concentration, and the relative masses of the constituents. Further, the composition of the precipitates as given in the tables and curves considers the precipitate as anhydrous; unquestionably much water is combined in the gelatinous precipitates here studied, but owing to the lack of a method of getting at it quantitatively it has purposely been left unconsidered.

This work has a bearing on the subject of colloidal solution. Reference to a former paper will show that it is possible to form a

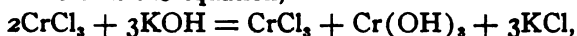
<sup>1</sup> Curves 1, 3, and 5 are taken from the thesis of V. J. Hall, *loc. cit.*

<sup>2</sup> C. E. Linebarger: *This Journal*, 17, 358 (1895).

<sup>3</sup> Taken from Table VI. A. V. E. Young, *loc. cit.*

<sup>4</sup> This work was done in 1896 and I have kept it back, hoping to make the data more complete; however, circumstances have not permitted of it, and do not at present. These results are of interest to those working on precipitation and solution, so I do not feel justified in withholding them longer.

colloidal solution containing chromium chloride, potassium chloride and potassium hydroxide all combined with each other and with water so that the equation,



does not represent the true state of the system. If any soluble sulphate be added, this colloidal solution gelatinizes. A nitrate or chloride will not produce this effect. It seems to me that this reaction disposes of the idea which had been advanced that *any electrolyte* will precipitate a colloid.<sup>1</sup> Here certainly the colloid seems to have a decided preference for sulphates.

#### BARIUM SULPHATE.

To examine further this "adhesion" phenomenon, samples of barium sulphate were prepared in two ways: (1) Precipitated with sulphuric acid from barium chloride dissolved in water, and the washed barium sulphate boiled for several hours with the aqueous solution of some metallic chloride. (2) Precipitated with sulphuric acid from an aqueous solution of barium chloride containing the same metallic chloride used in Method (1).

These samples enable one to decide whether the coloration of barium sulphate which is observed in samples precipitated in presence of salts of iron, manganese, chromium, etc., is necessarily enclosed when the crystal forms.

In this way I prepared samples of barium sulphate containing nickel, cobalt, manganese, chromium, iron and copper, and examined them under a high-power microscope. The crystals were measured by a stage and eye-piece combination micrometer, and averaged 0.00005 to 0.000125 inch in diameter.

No difference in shade could be detected between barium sulphate crystals prepared by Method (1) and those obtained by Method (2) with any of the metals used. The coloration was well marked and was compared with that of freshly prepared pure barium sulphate on the same glass slide.

These results indicate that the metals given can penetrate barium sulphate crystals after they are formed and find lodgment there. But once these metals are in the barium sulphate crystal it is, as every analyst knows, no easy matter to get them out. From this we might, without doing violence, argue for chemical combination between the barium sulphate and the metal (or its salt or oxide). Further, chromic chloride in aqueous solution is

<sup>1</sup> "Chromic Hydroxide in Precipitation," *loc. cit.*

known to dissolve barium sulphate crystals in appreciable amount. This shows that we have here a case of mutual action, the barium sulphate dissolving the chromium (in some form) and the chromium chloride in water dissolving the barium sulphate. As the barium sulphate remains solid, we have another case of a solid solution and a liquid solution coming into equilibrium in such a way as to give ground for believing that solid solution and liquid solution are of the same order, and to be classed as chemical combinations of solvent with solute.

I wish to thank Professor A. V. E. Young, of Northwestern University, for many helpful suggestions given me during the progress of this work.

CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN,  
MADISON, November 26, 1902.

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 65.]

## THE GRAVIMETRIC DETERMINATION OF MERCURY AND ITS SEPARATION FROM ARSENIC, ANTIMONY, AND COPPER.

BY CHARLES J. PRETZFELD.

Received December 2, 1902.

### HISTORICAL.

*Mercury Weighed as Chloride.*—For the determination of mercury in this form, the following reducing agents have been proposed: formic acid,<sup>1</sup> ferrous sulphate,<sup>2</sup> phosphorous acid,<sup>3</sup> glucose,<sup>4</sup> potassium hypophosphite,<sup>5</sup> a mixture of hypophosphorous acid and peroxide of hydrogen,<sup>6</sup> and hydrazine sulphate.<sup>7</sup>

*Mercury Weighed as Oxide.*—The determination of mercury in this form is unimportant, the only method known being that of Marignac.<sup>8</sup>

*Mercury Weighed as Metal.*—Under this heading, the history of mercury determination can be subdivided into three classes:

(A) By application of reducing agents in the cold.

<sup>1</sup> Bonsdorff : *Ann. Chem. Phys.*, 33, 78.

<sup>2</sup> Hempel : *Ann. Chem. Pharm.*, 110, 176.

<sup>3</sup> Rose : *Jsb. d. Chem.*, 13, 665.

<sup>4</sup> Hager : *Ztschr. anal. Chem.*, 17, 380.

<sup>5</sup> Thompson : *J. Soc. Chem. Ind.*, 16, 263.

<sup>6</sup> Vanino and Treubert : *Ber. d. chem. Ges.*, 30, 2608-2609.

<sup>7</sup> Jannasch and Durselen : Doctor's Dissertation at Heidelberg, 1899.

<sup>8</sup> *Jsb. d. Chem.*, (1849), p. 594.

(B) By application of heat to volatilize the mercury.

(C) By electrolytic deposition.

Under class *A* we have the methods of Mitscherlich,<sup>1</sup> Sieveking,<sup>2</sup> Jannasch and Alfiers,<sup>3</sup> and of Jannasch and Durselen.<sup>4</sup>

Under class *B* the methods of Milton,<sup>5</sup> Rose,<sup>6</sup> Eschka,<sup>7</sup> Attwood,<sup>8</sup> Schuyten,<sup>9</sup> Chism,<sup>10</sup> and of Janda<sup>11</sup> are the most important.

Under class *C* the most important methods are those of Hanay,<sup>12</sup> Clarke,<sup>13</sup> Ludwig and Classen,<sup>14</sup> Brand,<sup>15</sup> Vortman,<sup>16</sup> Rudorff,<sup>17</sup> Smith and Moyer,<sup>18</sup> Smith and Wallace,<sup>19</sup> Smith and Kollock,<sup>20</sup> Perreau,<sup>21</sup> and of Classen.<sup>22</sup>

#### EXPERIMENTAL.

About 8 liters of a solution of mercuric nitrate were made, and used for testing the accuracy of various methods for the determination of mercury. The strength of the solution was found to be, by electrolysis, such that each cubic centimeter contained 0.01673 gram of mercury.

*Estimation of Mercury as Sulphide.*—The form in which mercury is most commonly weighed being the sulphide, a few experiments were conducted to find how reliable this method is.

Twenty-five cc. of the solution of mercuric nitrate were taken and the mercury precipitated, and purified according to the method of Polstorff and Bulow. The solution was diluted to a volume of 250 cc. and saturated with sulphuretted hydrogen. The precipitate was washed with water containing sulphuretted

<sup>1</sup> *Pogg: Ann. Phys. Chem.*, 9, 39.

<sup>2</sup> *American Chemist*, 6, 160.

<sup>3</sup> *Ber. d. chem. Ges.*, Part II, pp. 2381-2385.

<sup>4</sup> Doctor's Dissertation at Heidelberg, 1899.

<sup>5</sup> *Erd. J.*, 37, 271.

<sup>6</sup> *Erd. J.*, 34, 36.

<sup>7</sup> *J. Chem. Soc. (London)*, (1872), p. 21.

<sup>8</sup> *Chem. News*, 39, 111.

<sup>9</sup> *J. Soc. Chem. Ind.*, 18, 475.

<sup>10</sup> *Trans. A. I. M. E.*, 28, 448.

<sup>11</sup> *J. Soc. Chem. Ind.*, 18, 610.

<sup>12</sup> *Am. Chem. J.*, 4, 193.

<sup>13</sup> *Chem. News*, 38, 273.

<sup>14</sup> *J. Chem. Soc. (London)*, 1, 493.

<sup>15</sup> *J. Soc. Chem. Ind.*, 8, 1011.

<sup>16</sup> *Jab. d. Chem.*, p. 2403.

<sup>17</sup> *Ztschr. angew. Chem.*, (1892), p. 5.

<sup>18</sup> *Ztschr. anorg. Chem.*, 4, 96.

<sup>19</sup> This Journal, 18, 169.

<sup>20</sup> Doctor's Dissertation, at Univ. of Penna., 1899.

<sup>21</sup> *J. Soc. Chem. Ind.*, 19, 53.

<sup>22</sup> "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 49.

hydrogen, and was then dissolved in a solution prepared by mixing a 15 per cent. solution of potassium sulphide with an equal volume of a 15 per cent. solution of caustic potash. The solution thus obtained was heated to 80° C. and upon addition of ammonium chloride, the mercury was reprecipitated as sulphide. This precipitate was washed with a solution of sulphuretted hydrogen, then twice with water, once with alcohol, twice with carbon bisulphide, and again with alcohol, dried at 100° and weighed.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> solution. Cc.	Calculated to Hg. Gram.	Weight of HgS found. Gram.	Calculated to Hg. Gram.
25	0.41825	0.4919	0.4239
19	0.31787	0.3734	0.3216
10	0.1673	0.1665	0.1693

*Estimation of Mercury as Chloride.*—The first method tried was that of Hempel, and was carried out as follows:

A known quantity of the standard solution of mercury was diluted to 150 cc.; 0.3 gram sodium chloride and 1.8 grams ferrous sulphate were then added and the solution stirred until the salts added had dissolved. Caustic soda was next added until the solution had become alkaline, and the whole was stirred for a few minutes. Sulphuric acid was then added to acid reaction and the solution again stirred. The solution was then allowed to stand over night. The precipitate was filtered off and washed once or twice with cold water, dried at 100° C., and weighed.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> Cl <sub>2</sub> . Gram.	Calculated to Hg. Gram.
(A) 25	0.41825	0.4898	0.4161
(B) 25	0.41825	0.4896	0.4159
(C) 25	0.41825	0.4906	0.4167
(D) 25	0.41825	0.4905	0.4166
(E) 17	0.2844	0.3355	0.2849
(F) 15	0.2509	0.2926	0.2490

The next method tried was that of Vanino and Treubert, in which an excess of sodium chloride is added to the solution of mercury, which should have a volume of about 100 cc., and then as a reducing agent a slight excess of a mixture containing one drop of commercial hypophosphorous acid to every cubic centimeter of peroxide of hydrogen is added drop by drop, while stirring. The solution is allowed to stand one hour, filtered on balanced filters



and quickly washed with hydrochloric acid, and finally with water. The temperature used for drying was 105° C.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> Cl <sub>2</sub> . Gram.	Calculated to Hg. Gram.
25	0.41825	0.4893	0.4156
25	0.41825	0.4892	0.4155
21	0.35133	0.4105	0.3486
10	0.16730	0.1955	0.1660
15	0.25096	0.2937	0.2494

By a slight modification of this method, very accurate results were obtained. Instead of converting the mercury and then reducing, the reducing agent was added first and after stirring for about one minute, an excess of sodium chloride was added. A heavy curdy precipitate, very similar in appearance to that of silver chloride, was thrown down immediately and settled very rapidly. The other conditions of the above method were maintained. The accuracy of the results obtained in this manner can be judged from the following table.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> Cl <sub>2</sub> . Gram.	Calculated to Hg. Gram.
13	0.21749	0.2556	0.2171
19	0.31787	0.3736	0.3173
15	0.25095	0.2951	0.2506
15	0.25095	0.2953	0.2508
10	0.16730	0.1972	0.1675
10	0.16730	0.1972	0.1675
10	0.16730	0.1971	0.1674

The explanation for the rapid formation of this precipitate, is that mercury in the form of nitrate is reduced, and this salt of mercury being much more dissociated than the chloride, the reaction takes place in a much shorter period of time. The disadvantage of the above is, however, that mercury is usually in the form of chloride, and for this reason the method cannot be applied very generally.

The next method tried was that of H. Rose. It was conducted in exactly the same manner as that of Vanino and Treubert, the only difference being that phosphorous acid is used as a reducing agent, and that the precipitate was allowed to settle over night. The results are quite low, probably due to the strong reducing action of phosphorous acid. The precipitate had a grayish color

and also showed a tendency to run through the paper. The results obtained are as follows:

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> Cl <sub>2</sub> . Gram.	Calculated to Hg. Gram.
25	0.4182	0.4881	0.4146
14	0.2342	0.2726	0.2316
17	0.2844	0.3311	0.2812
13	0.2175	0.2530	0.2149
17	0.2844	0.3313	0.2814
20	0.3346	0.3913	0.3324

When the reducing agent was added before converting the mercury to chloride, the following results were obtained:

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> Cl <sub>2</sub> . Gram.	Calculated to Hg. Gram.
10	0.1673	0.1970	0.1673
15	0.2509	0.2959	0.2514
10	0.1673	0.1968	0.1671
10	0.1673	0.1963	0.1667

The quality of the precipitate obtained in this way was the same as that obtained by similarly modifying Vanino and Treubert's method.

*Estimation of Mercury as Arsenate.*—Since the percentage of mercury in mercury arsenate is smaller than in mercury sulphide or chloride, the error caused by manipulation will of course be smaller than if the mercury formed a larger proportion of the precipitate. That an arsenate of mercury exists, is known,<sup>1</sup> but no attempt had ever been made to weigh the mercury in this form. Those conditions were consequently sought which would precipitate the metal completely and give the most accurate results. By the following method good results were obtained. To a cold solution of mercuric nitrate, of a bulk of about 100 cc., about 20 cc. of a saturated solution of sodium arsenate was added, this being an excess. A heavy yellowish-white precipitate of mercuric arsenate was immediately formed, and settled rapidly, but in order to insure complete precipitation, it was found best to allow the solution containing the precipitate to stand for about five hours. The solution was then filtered through balanced papers, and the precipitate was washed with cold water, dried at 95° C. to 100° C. and weighed.

<sup>1</sup> Dammer's "Anorganische Chemie," II, p. 921.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Weight of Hg <sub>2</sub> (AsO <sub>4</sub> ) <sub>2</sub> Gram.	Precipitate calcula- ted to Hg. Gram.
15	0.2509	0.3674	0.2509
15	0.2509	0.3677	0.2512
15	0.2509	0.3671	0.2508

These results are sufficiently accurate for any requirements, and the method is extremely simple. Unfortunately, however, the mercury is not precipitated as arsenate from a chloride solution, thus limiting the application of the method considerably. The presence of a small amount of free nitric acid did in no way interfere with the accuracy of the results.

*Electrolytic Determination of Mercury.*—Two methods only were used, the purpose having been more to determine the strength of the standard solution used, than to compare the methods.

In the first method the conditions proposed by E. F. Smith were tried.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> Cc.	KCN. Gram.	Dilution. Cc.	Current.	Voltage.	Tem- perature. °C.	Mercury found. Gram.
10	0.8	100	N.D. <sub>100</sub> = 0.07 A	3.2	65	0.1675
10	0.8	100	N.D. <sub>100</sub> = 0.07 A	3.2	65	0.1663

The other method was from a solution of the double sulphide of mercury and potassium. The conditions and results were:

Hg(NO <sub>3</sub> ) <sub>2</sub> Cc.	K <sub>2</sub> S. Cc.	Dilution. Cc.	Current.	Voltage.	Tem- perature. °C.	Mercury found. Gram.
10	20-25	125-130	N.D. <sub>100</sub> = 0.12 A	2½	70	0.1672
10	20-25	125-130	N.D. <sub>100</sub> = 0.12 A	2½	70	0.1673

From these results, the strength of the solution in terms of mercury was 0.01673 gram for each cubic centimeter.

All of the most important methods for the gravimetric estimation of mercury having been tried, it was concluded that, when accuracy is desired, the following methods, only, will give satisfactory results.

First, the method of Vanino and Treubert, as modified, page 201.  
Second, the method of Rose, as modified, page 201.

Third, the determination of mercury as arsenate, described on page 202.

Fourth, the determination of mercury by electrolysis.

Unfortunately the first, second and third methods above re-

ferred to cannot be used when the mercury is in the form of chloride, the first and second yielding low results, and the third being impossible since no precipitate is formed. The precipitation of mercury as sulphide, on the other hand, permits of very wide application. The precipitation as such is always rapid as well as complete, but if weighed in this form it yields high results on account of the separated sulphur present. The precipitation in this form is however of great value, not only because it acts in many cases as a separation, but also because the precipitate can easily be dissolved and electrolyzed from the solution thus obtained, yielding most satisfactory results. This method was used in the succeeding work on the separation of mercury.

*The Separation of Mercury from Arsenic, Antimony and Copper.*—The most important methods for this separation are those of Rose,<sup>1</sup> Fresenius,<sup>2</sup> Polstorff and Bülow,<sup>3</sup> v. Uslar,<sup>4</sup> Jannasch and Lenhert,<sup>5</sup> Jannasch and Devin,<sup>6</sup> and Jannasch and Durselen.<sup>7</sup>

As these methods either afford low results or require an excessive amount of manipulation, a simpler and more accurate method was sought.

#### EXPERIMENTAL.

##### *Separation of Mercury from Antimony and Copper by the Use of Sulphuretted Hydrogen in a Cyanide Solution.*

*Separation of Mercury from Copper.*—Although it was already known that mercury could be separated from copper by saturating a cyanide solution of the two metals with sulphuretted hydrogen,<sup>8</sup> no attempt has been made to separate mercury from antimony and arsenic by a method based on the same, or on a similar principle. Before going further, it was considered advisable to test the accuracy of the method of Haidlen and Fresenius for the separation of mercury from copper. The results were found to be satisfactory.

<sup>1</sup> *Jsb. d. Chem.*, 13, 665.

<sup>2</sup> *Ztschr. anal. Chem.*, 2, 343 (1863).

<sup>3</sup> *Ibid.*, 31, 697.

<sup>4</sup> *Ibid.*, 34, 411.

<sup>5</sup> *Ztschr. anorg. Chem.*, 12, [5], 359-364.

<sup>6</sup> *Ber. d. chem. Ges.*, 31, 2, 2377-2385.

<sup>7</sup> Doctor's Dissertation, Heidelberg, 1899; *Ibid.*, Heidelberg, 1899.

<sup>8</sup> Haidlen and Fresenius: *Ann. Chem. Pharm.*, 43, 144 (1842).

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Hg(NO <sub>3</sub> ) <sub>2</sub> calcu- lated to Hg. Gram.	Cu taken. Gram.	Hg found. Gram.
9	0.1505	0.05	0.1497
10	0.1673	0.05	0.1666
10	0.1673	0.05	0.1670
10	0.1673	0.05	0.1667
10	0.1673	0.15	0.1672
10	0.1673	0.15	0.1674
10	0.1673	0.30	0.1671
10	0.1673	0.30	0.1670

*Separation of Mercury from Antimony and Copper.*—The above method was tried for the separation of mercury from solutions containing antimony and copper, and although good results were obtained, the process was inconvenient owing to the partial precipitation of antimony, upon adding potassium cyanide. In the presence of tartaric acid, it was found that antimony remains completely in solution and that upon saturating the solution with sulphuretted hydrogen, only mercury is precipitated.

*Separation of Mercury from Antimony, Arsenic and Copper by the Use of Tartaric Acid, Potassium Cyanide and Sulphuretted Hydrogen.*

*Separation of Mercury from Antimony and Copper.*—To a clear solution of the three metals, about 30 cc. of a saturated solution of tartaric acid was added and the solution stirred for one or two minutes. Potassium cyanide was then added in small amounts at a time, until the solution became clear. While adding the latter reagent, it was found necessary to stir the solution continually in order to dissolve the potassium cyanide. Hydrogen sulphide was then led into the solution, until saturated, and the precipitate of mercury sulphide was allowed to settle. This precipitation was performed in the cold, as there is some danger of losing a little mercury with the escaping fumes. The precipitate of mercury sulphide was then filtered, dissolved and electrolyzed.

## RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	Sb taken. Gram.	Cu taken. Gram.	Hg found. Gram.
10	0.1673	0.10	0.10	0.1672
10	0.1673	0.10	0.10	0.1665
8	0.1338	0.20	0.20	0.1328
9	0.1505	0.20	0.20	0.1509
11	0.1840	0.30	0.30	0.1840
12	0.2007	0.30	0.30	0.2005
9	0.1505	0.10	0.30	0.1510
10	0.1673	0.10	0.30	0.1669
8	0.1338	0.30	0.10	0.1339
11	0.1840	0.30	0.10	0.1844

The conditions for this separation were found to be very broad, thus rendering the method one which can be carried out with great facility. The minimum amount of potassium cyanide required is an excess of 1 or 2 grams. It is safer to add an excess of 2 or 3 grams so that the solution will be strongly alkaline. Any excess beyond this amount does no harm. The dilution also permits of wide limits. The smallest bulk which was used in the above determinations was about 150 cc. and the largest about 500 cc. In both of these experiments the results were accurate. Furthermore, the solution, alkaline with potassium cyanide, was allowed to stand for more than two hours, with no perceptible change. Nor did standing for two or three hours after precipitation with hydrogen sulphide interfere in any way with the final result. The advantage of the tartaric acid in the solution, over the method first attempted, where no tartaric acid was used, is firstly, that no precipitate of antimony is formed, thereby avoiding the necessity of an additional filtration, and in case a determination of antimony is required, the solution of this precipitate is avoided. The red color formed in the former method is completely absent in the presence of this acid. In most, if not all cases, however, the solution becomes pale orange, which is not in the least an objection. Again when no tartaric acid is used, it is always fatal to use potassium cyanide, containing sulphur<sup>1</sup> since mercury is precipitated as sulphide and is consequently filtered off with the antimony and copper. When, on the other hand, tartaric acid is present, a black precipitate of mercury sulphide is formed which can be filtered off with the main precipitate of mercury sulphide, precipitated by hydrogen sulphide.

*Separation of Mercury from Arsenic, Antimony and Copper.—*

The next separation attempted under these same conditions was the separation of mercury from arsenic. A solution of sodium arsenate was made up of a strength of about 1 per cent. of metal. The results of the separations were very satisfactory.

RESULTS.

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Cc.	Calculated to Hg. Gram.	As taken Gram.	Hg found. Gram.
8	0.1338	0.05	0.1342
10	0.1673	0.05	0.1670
11	0.1840	0.30	0.1833
9	0.1506	0.30	0.1511

<sup>1</sup> Potassium cyanide free from sulphur is a very expensive reagent.

To determine if mercury could be separated from antimony, arsenic and copper, experiments were made with the following results :

Hg(NO <sub>3</sub> ) <sub>2</sub> taken. Gm.	Calculated to Hg. Gram.	Cu taken. Gram.	Sb taken. Gram.	As taken. Grain.	Hg found. Gram.
9	0.1506	0.05	0.05	0.05	0.1509
9	0.1506	0.05	0.05	0.05	0.1507

It was also attempted to separate mercury from tin but the results were very low. This, although it could not be accounted for, is of interest, since, in the method of Polstorff and Bülow where mercury is separated by dissolving the sulphide in alkaline sulphide and then reprecipitating it as sulphide on addition of ammonium chloride, some mercury is also withheld by tin if present.<sup>1</sup> The method of v. Uslar,<sup>2</sup> in which phosphorous acid is used to separate mercury from the metals of the fifth and sixth group is useless also, if tin is present. Bismuth and lead, if present, are completely precipitated with the mercury as sulphides, from which they are separated by digestion with an alkaline sulphide.

#### MERCURIAL ORES.

*A. Analysis of Cinnabar.*—Cinnabar, being the most important ore of mercury, it seemed well worth while to compare one or two of the most important methods for the determination of that metal therein.

The most important methods for the determination of mercury in cinnabar are those of Classen,<sup>3</sup> Rising and Lenher,<sup>4</sup> Smith and Wallace,<sup>5</sup> Chism<sup>6</sup> and a number of distillation methods.

By the method of Smith and Wallace, the ore was found to contain 16.0 per cent. and 16.02 per cent. of mercury. Chism's method was tried with various modifications, yielding the following results :

Ore taken. Gram.	Hg found. Per cent.
0.29755	13.81
0.22440	13.68
0.1661	15.35
0.1301	15.14
0.1384	15.32
0.1384	13.87
0.4625	13.91

<sup>1</sup> Classen : "Ausgewählte Methoden der Analytischen Chemie," p. 63.

<sup>2</sup> *Ztschr. anal. Chem.*, 24, 391 (1895).

<sup>3</sup> "Ausgewählte Methoden der Analytischen Chemie," Ed. 1901, p. 50.

<sup>4</sup> *This Journal*, 18, 96 (1896).

<sup>5</sup> *Ibid.*, 18, 169 (1896).

<sup>6</sup> *Trans. A. I. M. E.*, 28, 148 (1898).

Another method tried on cinnabar was the distillation of a large amount of mercury from the ore, which had been mixed with iron filings. An ordinary glass retort was used and the mercury was caught in very dilute hydrochloric acid. The purification of the mercury was carried out by treatment with successive portions of dilute hydrochloric acid. It was finally poured into a weighed porcelain crucible and dried after having been washed with alcohol, two or three times.

## RESULTS.

Ore taken. Grams.	Iron filings taken. Grams.	Hg found. Grams.	Hg found. Per cent.
22.5214	175	3.5163	15.61
24.1709	180	3.7402	15.47

*B. Analysis of Mercurial Tetrahedrite.*—Although earnest and repeated efforts were made to procure specimens of mercurial tetrahedrite, the only one that could be obtained contained but 0.3 per cent. of mercury. This was considered too low to show a just comparison of the methods, so a mixture of cinnabar and tetrahedrite was made and analyzed in the same way.

In applying the method in which tartaric acid and potassium cyanide are used, the decomposition of the mineral and mixture were effected in the manner described by Rose and Wöhler. The solution obtained was then filtered. To the filtrate, tartaric acid was added, then potassium cyanide and this was followed by the addition of sulphuretted hydrogen. The precipitate of mercuric sulphide was then filtered from the solution and treated as already described. If lead and bismuth are present, they also will be precipitated and can be separated from the mercuric sulphide by any of the well-known methods. All of the other metals likely to be found in tetrahedrite remain in solution.

## RESULTS.

Amount of mineral taken. Gram.	Mercury found. Gram.	Mercury. Per cent.	
0.9153	0.0012	0.13	} Method of Rose and Wöhler.
1.0474	0.0014	0.13	
1.0500	0.0015	0.14	
1.1986	0.0042	0.35	} Tartaric acid and potas- sium cyanide method.
1.0278	0.0039	0.38	
0.8581	0.0756	8.81	} Method of Rose and Wöhler.
0.8989	0.0805	8.95	
1.0310	0.0931	9.03	
0.8853	0.0845	9.54	} Tartaric acid and potas- sium cyanide method.
0.9139	0.0874	9.56	
0.8592	0.0814	9.47	



These results show conclusively that the separation of mercury from arsenic, antimony, and copper, by the use of tartaric acid and potassium cyanide is more complete and consequently more accurate than by the use of ammonium sulphide.

Chism's method also was tried on the tetrahedrite, with good results. This seems to prove this method very good for ores running low in mercury.

The results obtained by Chism's method were 0.27 per cent. and 0.33 per cent. of mercury.

As this work was carried out under the suggestion and guidance of Professor E. H. Miller, it is but just and proper, that any merit which it may possess be associated with his name.

QUANTITATIVE LABORATORY,  
May, 1902.

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## NOTE CONCERNING THE CALCULATION OF THERMOCHEMICAL RESULTS.

BY THEODORE WILLIAM RICHARDS.

Received December 10, 1902.

It is well known that the heat capacities of the majority of reacting substances change during their reaction. The magnitude of these changes and their significance are nevertheless often neglected.

A serious error may arise from this neglect. For example, according to the results of Thomsen, the neutralization of an approximately half normal solution of sodium hydroxide by an equivalent solution of hydrochloric acid involves an increase of heat capacity of 1.27 per cent.<sup>1</sup> The question now arises, since the solutions themselves are the capacities being warmed, What value for the total heat capacity shall be used in the calculation of the heat of reaction? Obviously the energy-change will be found to be 1.27 per cent. greater if the final, rather than the initial, heat capacity is used. The answer to this question is variously given in the different authorities upon thermochemistry. Ostwald and Luther in their admirable handbook<sup>2</sup> use the sum of the initial heat capacities; Thomsen often uses the capacity of the water alone; Berthelot commonly considers the capacity as equal to that

<sup>1</sup> Thomsen : "Thermochemische Untersuchungen," I, p. 67 (1882).

<sup>2</sup> Ostwald-Luther : *Physiko-Chemische Messungen*, (1902), p. 214.

of the same volume of water, and Wiedemann and Ebert,<sup>1</sup> as well as Traube,<sup>2</sup> recommend similar crude approximations.

It is probable that all of these writers understood wholly the conditions involved by their respective methods, but it is certain that they have not made this understanding clear to the public. The resulting frequently observed confusion among students of physical chemistry concerning this point has therefore led to the present paper. This paper does not pretend to claim originality; it is designed rather to further a general comprehension of the subject, and thus to add to precision of work and statement.

Obviously, since changing heat capacity means changing heat of reaction with changing temperature,<sup>3</sup> the precise thermochemical reaction should be conducted isothermally. In many cases, Waterman's method, which consists in dropping into a warming mixture known weights of cold material and vice versa,<sup>4</sup> may make this isothermal performance possible. Here the calculation is very simple, for the heat capacity to be considered is merely that of the compensating foreign material,—unless indeed this substance in the act of mixing changes its own heat capacity. Waterman's method is, however, rarely employed; the more usual method is to allow the reacting substances to raise or lower the temperature of their resulting mixture adiabatically, that is, without releasing or gaining heat. Nothing could be simpler than the calculation of this adiabatic process in terms of an isothermal one; and this calculation at once clears away the confusion before mentioned.

Imagine for the sake of definiteness a warming reaction. According to the first law of energy, the isothermal evolution of heat in the reaction may be as well measured in two stages as in one. Hence, after the reaction is completed without loss of heat, the mixture may be cooled down to the original temperature; and the heat given out during this cooling will be the total heat of reaction at that temperature. This value will be found by multiplying the heat capacity of the *product* of the reaction by the change of temperature, since it is this product which is to be cooled.

The proceeding may be represented graphically by the right-

<sup>1</sup> Wiedemann-Ebert: *Physikalisches Praktikum* (1899).

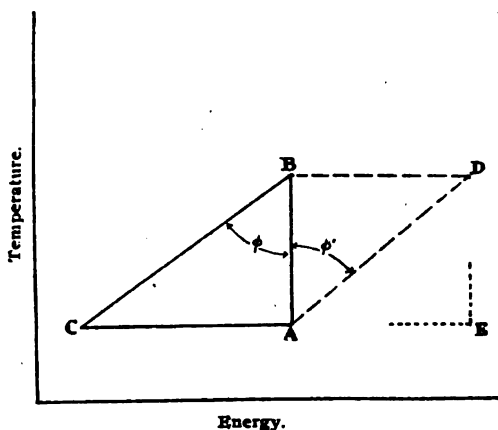
<sup>2</sup> Traube's (trans. Hardin): "Physical Chemical Methods," 1898.

<sup>3</sup> Kirchhoff's Law; see also Thomsen: "Thermochemische Untersuchungen," I, p. 65 (1882).

<sup>4</sup> Waterman: *Phys. Rev.*, 4, 161 (1896); see also Cady: *Jour. Phys. Chem.*, 2, 361 (1898).

angled triangle A B C in the accompanying diagram, in which A represents the initial state of the system, A B the adiabatic process, B C the cooling process, and A C the desired isothermal loss of energy.

Does this demonstration, proving that the capacity of the *products* must be used in order to obtain the true heat of reaction at the initial temperature, render valueless a knowledge of the capacity of the *factors*? Not at all; for it is easy to show that the heat of reaction computed from the specific heats of the *factors* is that corresponding to the *final* temperature. Let us consider the



same reaction as before, between the same temperatures. The adiabatic effect will be precisely the same as before. But in order that the heat capacities of the factors may be used, and the total process still be isothermal, it is obvious that the factors must first be cooled from a temperature which is to be the final one, to that from which the adiabatic reaction is to start. This cooling, represented above by the line D A, is immediately followed by the adiabatic reaction A B, which brings the system to the same temperature as D. During this double process, the system at the final temperature has lost an amount of energy represented by D B, all of which was removed by the cooling of the factors.

In brief, *the total heat capacity of the product must be multiplied by the change in temperature in order to compute the heat of reaction at the initial temperature, while the total heat capacity of the factors must be so multiplied in order to compute the heat of reaction at the final temperature.* This statement applies to a cooling reaction as well as to a warming reaction. If, as is often

the case, the total energy change at an average temperature is desired, the average of the two total heat capacities must be used in the computation. If the two factors have at first different temperatures, their effects must be computed separately and the resulting heat of reaction must be referred to the final temperature. When there is an accidental outside warming or cooling effect, the corrected temperatures should be used.

A slight inexactness lies in the italicized statement, due to the fact that specific heat itself is variable with temperature. Therefore, the heat capacities of the initial and final systems are not in reality perfectly constant, and the lines B C and D A should not be perfectly straight. This deviation is nevertheless usually very slight in dilute aqueous solutions; and until the whole body of physicochemical data attains a much greater degree of accuracy than at present, it may be neglected.

Evidently the quadrilateral figure C A B D may be used to demonstrate trigonometrically the rule of Kirchhoff—the familiar relation which lies at the basis of the question treated in this paper. The reaction may proceed from A to B by two simple indirect paths. According to one, the reaction may be allowed to take place isothermally, at the lower temperature, involving the loss of energy, A C, and the products may then be warmed to a higher temperature involving a gain of energy, C B, while according to the other the factors may be warmed to the higher temperature, A D, and the reaction there allowed to proceed isothermally to B by the loss of energy, D B. In this demonstration it is of course unnecessary to place B exactly over A, a condition which ensues only when the higher temperature is that actually attained by the adiabatic reaction. Obviously, from inspection of the diagram,

$$CE = CA + AB \tan \phi' = BD + AB \tan \phi;$$

$$CA - BD = AB (\tan \phi - \tan \phi').$$

Now  $(CA - BD) = U_T - U_{T'}$ , the difference between the heats of reaction at the two temperatures;  $\tan \phi$  or  $\frac{CA}{AB}$  represents the heat capacity of the products ( $K_2$ );  $\tan \phi$  or  $\frac{BD}{AB}$  represents the heat capacity of the factors ( $K_1$ ); and the vertical distance AB represents the change of temperature. Hence this trigonometrical statement at once reduces to the well-known equation

$$K_2 - K_1 = \frac{U_T - U_{T'}}{t}.$$

An important object of the discussion is to emphasize the necessity of reducing all thermochemical data to their isothermal values at some definite convenient temperature (preferably  $20^{\circ}$ ), in order that they may be strictly comparable.

As an evidence of frequent laxity in this respect, the often quoted figures for the heat of neutralization of hydrochloric, hydrobromic and hydriodic acids may be cited. Thomsen records as the three values to be compared 13,740, 13,748, 13,676 calories<sup>1</sup> (or better, 57.46, 57.49 and 57.19 kilojoules), if the base is sodium hydroxide. On seeking the original data, it is easily found that the first corresponds to a rise of temperature from about  $18^{\circ}$  to  $22^{\circ}$ , the second to a rise from  $16.6^{\circ}$  to  $18.6^{\circ}$ , and the third to a rise from  $17.5^{\circ}$  to  $19.5^{\circ}$ . In the calculation, the approximate heat capacities of the factors were used in each of the three cases. If all these results are reduced to the isothermal value at  $20^{\circ}$ , the heats of neutralization become respectively 13,820, 13,690, and 13,650 calories (or 57.8, 57.2, and 57.1 kilojoules). The order of magnitude in the cases of hydrochloric and hydrobromic acids is reversed by the new calculation, and they have been separated by a whole per cent.<sup>2</sup> Even these values cannot be called ultimate, for the heat capacities of most of the solutions concerned are not accurately known, the value of Thomsen's centigrade degree in terms of the International Standard is not recorded, nor do we know how nearly the  $20^{\circ}$  points on the thermometers correspond with the true point.

It is hoped that these critical remarks will not be considered as depreciating the admirable and important work of Thomsen, Berthelot, and others. For many purposes the approximate values suffice, and if the greatest precision had been aimed at, the bulk of the results must have been much smaller, an outcome which would have been a real misfortune. In some cases the correction for cooling may have caused even a greater uncertainty than those considered above, and great care about heat capacity would have been labor thrown away. It is not at all surprising that this admirable work should not have attained a degree of

<sup>1</sup> "Thermochemische Untersuchungen," I, pp. 104, 155, 63, 67 (1882).

<sup>2</sup> The apparent inconsistency of the results on page 63 of Thomsen's work is easily explained by noting that there the heat capacity of the *product* was used in the calculation. The hydrochloric acid was in every case twice the strength of the other acids, hence the heats of dilution (which are, however, very small) should be included for an exact comparison.

accuracy sufficient for the more exacting needs of the present day.

In this connection it is appropriate to call attention to the fact that not all of the values for heat of reaction commonly given in the tables correspond to consistent atomic weights, although most of them are calculated upon the basis of  $O = 16.000$ . A praiseworthy service would be rendered by any careful computer who would take the trouble to recalculate all the data and express the results for  $20^{\circ} C$ . in terms of the most accurate table of atomic weights and the admirable c. g. s. unit of energy, the kilojoule, adopted by Ostwald.<sup>1</sup> The latter's preliminary tables, although an important step in the right direction, are much hampered in their usefulness by their limited scope and the frequent omission of significant decimals.

#### SUMMARY.

This paper is a plea for greater accuracy in the calculation of thermochemical data. The importance of a uniform temperature for comparison and consistent atomic weights are especially emphasized. It is shown that when the heat capacity of the factors is used in the calculation, the resulting heat of reaction corresponds to the final temperature attained, while if the heat capacity of the products is used in the calculation, the result corresponds to the initial temperature.

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#### NOTES.

*Note on the Occurrence of Alum as an Efflorescence on Bricks.*—Some time ago I was consulted as to the cause of the discoloration of certain white bricks used in the construction of a large office building in this city. It was readily ascertained to be due to the formation and subsequent oxidation of ferrous sulphate. To remove the stain, some of the bricks were treated with sulphuric acid and then thoroughly washed with water. After they had been dried, a white efflorescence appeared on their surface, and it was found to consist for the most part of potash alum. As I have not been able to find any reference to the occurrence of this salt among the sulphates which are known to exist in similar efflorescences, it occurred to me that a quantitative analysis of the product might be of interest.

Owing to the lack of material the analysis made was incom-

<sup>1</sup> Ostwald's "Grundriss der Allgemeinen Chemie," p. 253 (1899).

plete, but the results proved conclusively that the water-soluble portion, which crystallized in octahedra, was nearly pure potash alum.

HARRY F. KELLER.

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*Rapid Determination of Molybdenum in Steel.*—It has been found to be an improvement on the method previously described,<sup>1</sup> to use only 0.8 gram of drillings, and to make the precipitation in 200 cc. of the solution instead of 300 cc., taking only 100 cc. of the filtrate for reduction and titration. In this way an evaporation requiring more time than all the rest of the analysis put together is dispensed with. Reduction and titration should take place in small, and not in large volume of solution, on account of reduction not always being complete in the latter case, as is proved by the fact that Brakes<sup>2</sup> finds it necessary to use the old Emmerton factor. But if the separation be made in 200 cc. of solution, ammonia may not be used because the separation is an incomplete one with this reagent when made in a small volume of solution. The caustic soda solution is most easily made by dissolving 1 pound in 2000 to 2100 cc. water. 100 cc. of this solution is used in a determination.

Another improvement in the method (Brakes) is to expel the nitric acid used for the solution of the steel by adding 3 cc. of concentrated sulphuric acid and evaporating to fuming. The complete expulsion of the nitric acid is very important, and care must be taken that none remains on the cover, since nitrous acid or other reducing compounds are formed when a solution containing nitric acid is passed through the reductor. The results obtained by Brakes<sup>3</sup> indicate that chromium does not interfere with the determination when a sulphuric acid solution is used.

GEORGE AUCHY.

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### NEW BOOKS.

**ELEMENTARY CHEMISTRY.** BY L. M. DENNIS AND F. W. CLARKE. New York: The American Book Company. 1902. 340 pp. **LABORATORY MANUAL** to accompany the above. 254 pp. Interleaved.

The matter treated in this book is essentially the same as that to be found in most other works of its class. The mode of treatment is not especially novel. It is in fact less so than in several

<sup>1</sup> This Journal, 24, 273.

<sup>2</sup> J. Soc. Chem. Ind., 21, 832.

<sup>3</sup> Loc. cit.

recent High School texts. Thus the atomic and molecular theories make their début within ten pages from the beginning, while the principle of definite proportion is reached on page 59. Even when this law appears, the phraseology suggests a dogma rather than a result of observation. Instead of demonstrating the building up of an equation from quantitative experiments, the authors show (p. 69) how, given the equation, we may calculate the results of an experiment *before* its actual performance.

The "two-volume law" (p. 96), which is not a "law" (that is, a general truth) at all, as the writers themselves tacitly acknowledge later, is used as the foundation of an elaborate proof that if we take the molecular weight of a compound and halve it, we get the density. This derivation of facts from theoretical considerations is typical of the way in which the principles of the science are handled in the book. Presently the compounds of carbon are used for illustration and the molecular weights of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , etc., are shown to give the densities when they are divided by 2. The authors add: "In a similar way we can investigate the volatile compounds of other non-volatile elements, and prove that the two-volume law above indicated is of universal application." They have overlooked the fact that in taking the molecular weights 28 and 26 for ethylene and acetylene they were assuming the very law which they afterward hold their illustration to have proved. The maintenance of the distinction between fact and theory is the most difficult task of the teacher of chemistry. Even trained chemists find it hard. It seems to the reviewer that the present book fails to make this distinction sufficiently clear. The promise of inductive and rational treatment made in the preface is belied by much of the contents, and that at the most vital points.

The book is marred by the presence of a number of incorrect or unfortunately worded statements, such as, that when iron burns in oxygen, the melted *metal* drops to the bottom of the bottle; that ozone has a suffocating odor; that hydrogen peroxide contains "exactly twice as much oxygen" as water; that "as a solvent, water far *exceeds* every other liquid known"; and so forth. The laws "govern" regally instead of existing only so long as they are "good". The resurrection of the electrochemical series of Berzelius is strange in view of the fact that modern research has given us the means of placing the elements in the order of *chemical*



activity. Fortunately, or unfortunately, the explanation is so befogged with statements about electro-negativeness and electro-positiveness that no application, correct or incorrect, to chemical behavior is likely to be made.

The laboratory manual covers a great deal of ground. A few questions are appended to each experiment. Some quantitative experiments are given, but they are at the end of the book.

The typography, illustrations, and binding of both books are excellent.

ALEXANDER SMITH.

**DISINFECTION AND DISINFECTANTS. A PRACTICAL GUIDE FOR SANITARIANS. HEALTH AND QUARANTINE OFFICERS. BY M. J. ROSENAU, M.D.** Philadelphia: P. Blakiston's Son and Co. 353 pp. Price, \$2.00 net.

The author of this book is connected with the United States Marine Hospital Service, as Director of the Hygienic Laboratory, and has had abundant opportunity to observe practically what he has written about. The work is divided into six chapters of which the first three treat of the various disinfecting agents in general use. The opinions of the author in discussing the applicability and relative merits of the substances considered seem eminently sound and practical. The fourth chapter deals with means for destroying insects which carry diseases. The fifth chapter gives clear directions for disinfection of houses, ships, railway cars, furniture, clothing, books, etc., and is very satisfactory. The sixth and last chapter deals with the question of disinfection after special diseases, and for each one the most efficient treatment is suggested. The book is illustrated and is well printed. On the whole it may be recommended to those in need of information in this direction.

J. H. LONG.

**DIE ZERSETZUNG STICKSTOFFFREIER ORGANISCHER SUBSTANZEN DURCH BAKTERIEN. BY DR. O. EMMERLING.** Braunschweig: Friedrich Vieweg und Sohn. 141 pp. and 7 plates. Price, 4 marks.

This little book describes the important group of decompositions usually classed as fermentations in which the active agents are not true ferments, in the modern sense of the word, but bacteria. The best known examples of such reactions are the acetic, lactic, butyric and gummy fermentations, in which carbohydrates or their derivatives are the materials on which the bacteria work. The author discusses these changes and several

others and points out the conditions under which various by-products are formed. Attention is called to the complexity of several reactions usually described in the text-books as comparatively simple. It is interesting to note in this connection the large number of cases in which ethyl alcohol is produced.

The book is not intended to be more than a suggestive compilation of results scattered through the recent literature, but as pretty full references are given it will be found useful to chemists and bacteriologists who desire to gain an insight into this important field of investigation, to which the author himself has made several valuable contributions.

J. H. LONG.

G. BUNGE'S TEXT-BOOK OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. Translated by F. A. STARLING and edited by E. H. STARLING. Philadelphia : P. Blakiston's Son and Co. 1902.

Bunge's text-book still remains the most popular book on the subject. The fourth German edition, from which the second English is translated, is not much enlarged over the previous editions of the work. However, Bunge's aim was to give the general principles of the chemical side of animal physiology and pathology, and in this he succeeded most brilliantly. There are only a few questions that the author discusses in greater detail, but those are chapters of such general interest, that every biologist will read them with great pleasure, whether he does or does not accept the conclusions of the writer. Such are the chapters on vitalism and mechanism, also the chapter on alcohol. The importance for the animal organism of the mineral constituents of food is discussed by Bunge more than it has been by any other writer. The book as a whole presents in a very interesting and comprehensive form the most obscure problems of physiology, and can be recommended to those who desire to gain a general knowledge on the subject.

P. A. LEVENE.

ELECTRO-CHEMICAL ANALYSIS. BY EDGAR F. SMITH. Philadelphia : P. Blakiston's Son and Company. 1902. 199 pp.

The earlier editions of Professor Smith's work on electro-chemical analysis are so widely and favorably known as to render unnecessary any extended notice of this third edition, further than to call attention to the changes and additions that have been made by the author.

The chapters on sources, reduction and measurement of cur-

rent have been slightly changed, and descriptions of new forms of apparatus have been added. Several pages are then devoted to a most interesting and suggestive description of an electrochemical laboratory. Only a few alterations have been made in the historical section, but in the special part devoted to the determination of the metals the treatment has been greatly expanded. The references to literature that are here given under each heading have been brought down to date, and many new methods and improvements of old methods have been incorporated in the text. The chapter upon the separation of the metals has been entirely rewritten, and this part of the subject is presented in a most clear and systematic form.

Both the press work and the illustrations show decided advance over the earlier editions.

It is to be regretted that in a work otherwise so complete specific mention is not made of methods for the separation of certain of the metals through the maintenance of a constant voltage, for while it is true that up to the present time such procedure has not been so far developed as to be of material assistance to the analyst, it would yet be well to call the attention of the student to the work that has been done in this field and to the possibilities of its extension.

L. M. DENNIS.

**A COURSE IN QUALITATIVE CHEMICAL ANALYSIS.** BY F. P. VENABLE. Fourth edition, revised by ALVIN S. WHEELER. New York: University Publishing Company. 1902. 54 pp. Price, 60 cents.

The only novelty that the present edition of this book offers is the absence of any reference to recent theories of solution and chemical action. The authors believe, evidently, that qualitative analysis may be taught effectively in the old way.

The directions for the systematic examination of substances are given, clearly, but so concisely, that, without the constant help of an instructor, the student will fail to secure satisfactory tests and separations. This remark applies as well, however, to larger and more pretentious text-books, and the difficulty that it points out can not be easily avoided. An index would enhance the value of the book.

L. B. HALL.

**RECIPES FOR THE COLOUR, PAINT, VARNISH, OIL, SOAP, AND DRY-SALT-TERY TRADES.** Compiled by an Analytical Chemist. London: Scott, Greenwood, and Co. 1902. 336 pp. Price, \$3.50 net.

Books of this class serve two purposes: they supply information

to the ignorant, and ideas or suggestions to the experienced. Every book of the sort has some things in it which will not work, and as a rule, the recipes which will work are those which have been outgrown by the special trade which used them. But if they are good in themselves, they are valuable to the non-professional; and occasionally, though rarely, those which are no good at all set the professional to thinking along a new line; at least, this has been the reviewer's experience. This book is a rather unusually good book of the sort, judging, of course, from those things which the reviewer knows. The author judiciously remarks in his preface that "it is, of course, assumed that the users of these formulae have some acquaintance with methods of manipulating them, and that they will also exercise a little common-sense when applying them to their purposes". If they do that, they will omit some of them altogether; but in the varnishes, for example, most of the recipes will make some sort of varnish, and some of them are very good, such as the coach and cabinet varnishes, though they take as many days to dry as the author gives hours. In general, the formulae are more complicated than those commonly in use in this country, and a glossary would always be useful in a book of this sort, for names vary in different countries and places, though usually intelligible to an expert. We are all acquainted, for instance, with "mineral turpentine", but no one can fail to be pleased with the idea of thinning paint with "mineral tea rose oil" instead of deodorized benzine. The reviewer commends this book to such as like books of recipes, and indorses the advice of the author to use it with some common sense. A. H. SABIN.

**A COURSE IN MODERN ANALYSIS.** BY E. T. WHITTAKER, M.A. Cambridge: The University Press. New York: The Macmillan Co. xvi + 378 pp.

This book aims at presenting those portions of modern analysis, as based on the so-called imaginary or complex number, which "seem to be of greatest importance at the present time." Infinite series are considered in all their phases, and all those important series and functions which were developed by Fourier, Bessel, Lagrange, Legendre, Laplace, Gauss, Abel, etc., in their study of practical problems. It is a useful work for those who wish to make use of the most advanced developments of mathematical analysis in theoretical investigations of physical and chemical questions. ARTHUR S. HATHAWAY.

**GENERAL PRINCIPLES OF PHYSICAL SCIENCE : AN INTRODUCTION TO THE STUDY OF THE GENERAL PRINCIPLES OF CHEMISTRY.** BY ARTHUR A. NOYES. New York : Henry Holt & Co. 1902. viii + 172 pp.

While works on physical chemistry are rapidly multiplying, it is refreshing to encounter one which promises to be a distinct creation rather than a mere variation or even an improvement on its predecessors. As the present volume treats of certain parts of the subject only, an outline of its contents must be given. The first chapter, a brief one, deals mainly with the method of science. The second, also brief, discusses the fundamental concepts of physical science. The third chapter, occupying over 50 pages, treats of the general principles relating to matter. The fourth chapter, about 100 pages in length, is devoted to the general principles relating to energy. It is to be regretted that the preface does not offer any hope of the early appearance of the remaining sections dealing with the general theories of chemistry, the relations between physical properties and chemical composition, the principles relating to the occurrence and equilibrium of chemical changes, and the principles relating to the energy changes attending chemical changes.

Although the book does not deal with the whole subject of physical chemistry, it is complete in itself. While the value of the book lies largely in the sanity and symmetry of the whole treatment, a few specially excellent features may be mentioned. The unscientific patchwork of unharmonized definitions which does duty in most books on chemistry has at last been "scrapped," and it was high time that some one should undertake this task, and an inter-consistent set of definitions of the laws and terms of the science has been devised to take its place. Much care has been used in explaining the nature and relations of the various units employed in physical science. The conception of the intensity and capacity factors of the several forms of energy occupies the fundamental position in the treatment of energetics which it deserves, but has not yet received in most books in the English language. In the discussion of the laws of energetics (formerly thermodynamics), the author is remarkably successful in anticipating and avoiding or disposing of the stumbling blocks which most students of the subject encounter.

The whole treatment is scholarly in its methods and philosophical in its grasp, and at the same time it is extraordinarily

lucid. Nothing that can set each conception in the clearest light and in the most instructive relation to other conceptions seems to be forgotten. No one interested in the teaching or study of general or physical chemistry can afford to leave this book unread.

ALEXANDER SMITH.

**GALVANIC BATTERIES: THEIR THEORY, CONSTRUCTION, AND USE.** BY S. R. BOTTONE. London and New York: Whittaker and Co. 1902. xvi + 376 pp. Price, \$1.50.

The author states in his preface that this work contains a description of every known battery of any practical use along with data as to electromotive force, internal resistance, and adaptability to particular requirements. For those who may have occasion to use batteries instead of a dynamo as a source of current, the book will undoubtedly prove helpful. Although the author states that "In order to render the book useful from a scientific point of view, as well as under the practical aspect, the theory of the battery has been carefully gone into," no mention is made of theories advanced by Helmholtz and by Nernst, which have thrown such a flood of light upon the whole subject. The book is profusely illustrated and the descriptions of the construction and operation of the batteries clear and concise.

C. E. LINEBARGER.

**LABORATORY EXERCISES IN PHYSICS FOR SECONDARY SCHOOLS.** BY GEORGE R. TWISS, B.Sc., Head of the Department of Science in the Central High School, Cleveland, Ohio. New York: The Macmillan Co. 1902. xiii + 193 pp. Price, 80 cents.

This manual is characterized by thoroughness of treatment and carefulness of statement. The author believes that "A small number of exercises worked for all there is in them" is better than a large number carelessly and superficially performed. The author has succeeded well in this his attempt "*first*, to secure the thorough enforcement of some of the fundamental principles of the science, together with a view of the kind of thinking and experimentation by means of which the facts and principles of physics have been established; *second*, to develop habits of precision in observation, thought and expression; and *third*, to train the student in the acquisition of practical power and skill in the use of apparatus."

C. E. LINEBARGER.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### TENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED IN 1902.

BY F. W. CLARKE.

Received October 16, 1902.

DURING 1902 there has been a fair amount of activity in the determination of atomic weights, and some of the work published is highly important. One new metal, radium, appears as a definite element for the first time, taking its proper place in the periodic system as a member of the calcium, strontium, barium group. The recorded investigations are summarized below. The work on iodine, calcium, selenium, lanthanum, and uranium is especially worthy of notice.

#### IODINE.

In order to establish more exactly the relative positions of tellurium and iodine under the periodic law, Ladenburg<sup>1</sup> has re-determined the atomic weight of the latter element. His process consisted in transforming silver iodide to silver chloride, by heating in chlorine, and a preliminary series of experiments gave the following results. All weights were reduced to a vacuum, and the calculations are based upon  $O = 16$ .

<sup>1</sup> *Ber. d. chem. Ges.*, 35, 2275.

Weight AgI.	Weight AgCl.	Atomic weight I.
31.2558	19.0817	126.93
33.7357	20.5930	126.96
49.88229	30.4525	126.94
47.8830	29.2262	126.98
60.1435	36.7154	126.95
41.3649	25.2448	127.01
50.8916	31.0664	126.95
41.3233	25.2200	126.98
80.8139	49.3181	127.02
89.5071	54.6367	126.96
		Mean, 126.97

This value is notably higher than that given by Stas, 126.85, and therefore additional determinations were necessary. Three experiments, conducted with the utmost care and with all needful precautions, gave as follows:

Weight AgI.	Weight AgCl.	Atomic weight I.
62.6608	38.2496	126.957
63.8351	38.9656	126.961
74.7516	45.6288	126.963
		Mean, 126.960

This result serves to vindicate the preliminary series, but the cause of the difference from Stas' value is yet to seek. One careful experiment by Stas' method, the synthesis of silver iodide, was made by Ladenburg, whose data, with all corrections applied, are these:

50.3147 Ag gave 109.4608 AgI. Hence  $I = 126.87$ .

Here Stas is corroborated, and the difference is evidently due to the different methods. Ladenburg regards the synthesis of the iodide from silver as attended by much greater errors than affect the other method, and says that their tendency is to lower the apparent atomic weight of iodine. The new data, therefore, are entitled to very respectful consideration.

Two syntheses of silver iodide are also given by Scott,<sup>1</sup> incidentally to his research upon tellurium. The data are subjoined, and represent reductions to a vacuum, and calculations based upon  $O = 16$  and  $Ag = 107.93$ .

Weight Ag.	Weight AgI.	Atomic weight I.
4.6240	10.0634	126.96
6.39978	13.92913	126.98

<sup>1</sup> *Proc. Chem. Soc. (London)*, 18, 112, May 7, 1902.



Here again there is a variation from Stas, and an agreement with the higher value obtained by Ladenburg. It seems clear that the atomic weight of iodine should be most carefully scrutinized.

#### CALCIUM.

An important preliminary notice by Richards<sup>1</sup> describes a number of experiments upon the atomic weight of calcium. The compound studied was the chloride, and the results, reduced to a vacuum, were as follows: (O = 16, Cl = 35.455.)

Weight CaCl <sub>2</sub> .	Weight AgCl.	Atomic weight.
1.56454	4.0409	40.121
3.57630	9.2361	40.130
3.59281	9.2788	40.129
5.00880	12.9364	40.124
9.00246	23.2506	40.125
		Mean, 40.126

Still another paper upon this subject, by Hinrichsen,<sup>2</sup> is supplementary to the memoir which he published in 1901.<sup>3</sup> Transparent calcite from Russia was reduced to lime by ignition. After reduction to a vacuum and correction for known impurities in the original material, the subjoined data were obtained.

Weight CaCO <sub>3</sub> .	Weight CaO.	Atomic weight.
31.20762	17.49526	40.139
22.00588	12.33642	40.136

The value found in 1901 was Ca = 40.142. These figures harmonize with those of Richards, and prove that the formerly accepted number, Ca = 40, is too low.

#### SELENIUM.

Atomic weight redetermined by Julius Meyer.<sup>4</sup> Silver selenite, scrupulously pure, was analyzed electrolytically. The data, with all weights reduced to a vacuum, are as follows:

Weight Ag <sub>2</sub> SeO <sub>3</sub> .	Weight Ag.	Per cent. Ag.	Atomic weight.
0.5152	0.3241	62.907	79.28
0.5237	0.3295	62.915	79.24
1.8793	1.1826	62.928	79.17
2.1460	1.3503	62.922	79.20
1.6964	1.0672	62.910	79.27
			Mean, 79.23

<sup>1</sup> This Journal, 24, 374.

<sup>2</sup> *Ztschr. phys. Chem.*, 40, 746.

<sup>3</sup> *Ibid.*, 39, 311.

<sup>4</sup> *Ztschr. anorg. Chem.*, 31, 391; *Ber. d. chem. Ges.*, 38, 1591.

From the sum of the weights, corrected for a trace of silver which remained in solution after electrolysis, the final result becomes

$$\text{Se} = 79.21.$$

This figure is nearly in accord with Lenher's determination, but notably higher than that obtained by Pettersson and Ekman.

#### TELLURIUM.

Guthier,<sup>1</sup> in order to determine the atomic weight of tellurium, has studied telluric acid and tellurium dioxide. His analyses depended upon the precipitation of tellurium by hydrazine hydrate, and special precautions were taken to avoid any oxidation of the precipitated metal. The latter was found to be extremely oxidizable. First, two direct determinations were made of water in telluric acid, as follows:

Weight $\text{H}_2\text{TeO}_6$ .	Weight $\text{H}_2\text{O}$ .	Per cent. $\text{H}_2\text{O}$ .	Atomic weight.
0.4937	0.1162	23.54	127.60
0.9910	0.2335	23.56	127.70
			Mean, 127.65

All weights were reduced to a vacuum, and calculations were based upon  $\text{O} = 16$  and  $\text{H} = 1.008$ .

Secondly, Guthier gives six determinations of tellurium in telluric acid, after several fractional crystallizations of the latter. Three separate fractions were studied, with duplicate determinations on each. The data are given below:

Weight $\text{H}_2\text{TeO}_6$ .	Weight Te.	Per cent. Te.	Atomic weight.
0.9380	0.5204	55.48	127.20
0.4963	0.2754	55.49	127.25
1.0485	0.5829	55.60	127.80
0.8865	0.4915	55.44	127.00
0.4339	0.2411	55.56	127.60
0.3492	0.1937	55.48	127.34
			Mean, 127.365

From tellurium dioxide, similarly reduced, the following data were obtained.

Weight $\text{TeO}_2$ .	Weight Te.	Per cent. Te.	Atomic weight.
0.1662	0.13287	79.94	127.50
0.3136	0.2507	79.94	127.50
0.2799	0.2238	79.95	127.60
			Mean, 127.53

<sup>1</sup> *Ann. Chem. (Liebig)*, 320, 52.

The average of the three series of determinations is

$$\text{Te} = 127.51.$$

The low results of the second series are probably ascribable to traces of mother-liquor retained in some crystals of the telluric acid.

A preliminary notice upon the atomic weight of tellurium has also been published by Scott.<sup>1</sup> The substances studied were trimethyl tellurium iodide,  $\text{Te}(\text{CH}_3)_3\text{I}$ , and the corresponding bromide. Analyses of the iodide were as follows:

Weight $\text{Te}(\text{CH}_3)_3\text{I}$ .	Weight AgI.	Atomic weight.
1.7461	1.3688	127.70
6.6425	5.20575	127.66
8.0628	6.3181	127.69

The bromide was titrated with silver solution, and gave these results:

Weight $\text{Te}(\text{CH}_3)_3\text{Br}$ .	Weight Ag.	Atomic weight.
2.4294	1.0373	127.77
6.8424	2.9201	127.78

The second sample of bromide was not so pure as the first. Rejecting it, the mean of the other four determinations gives  $\text{Te} = 127.70$ . The mean of all five is 127.74. All weights are reduced to a vacuum, and the antecedent values are  $\text{O} = 16$ ,  $\text{C} = 12.00$ ,  $\text{H} = 1.0075$ ,  $\text{I} = 126.85$ ,  $\text{Br} = 79.95$ ,  $\text{Ag} = 107.93$ .

#### LANTHANUM.

The determinations of atomic weight by Jones<sup>2</sup> were made upon material of remarkable purity. The only contamination which could be detected with the Rowland spectroscope of the Johns Hopkins University, was a trace of cerium, amounting to not more than 0.01 per cent. and probably much less. Furthermore, some of the lanthanum oxide was ignited in hydrogen in order to make sure that no oxide higher than  $\text{La}_2\text{O}_3$  was present. The method of determination was the usual synthesis of sulphate from oxide, and careful experiments showed that under the conditions of the investigation no acid sulphate was formed. The sulphate which was finally weighed was perfectly soluble in water and absolutely neutral in reaction. Twelve determinations are given, as follows: The atomic weight was calculated with  $\text{O} = 16$ , and  $\text{S} = 32.06$ .

<sup>1</sup> *Proc. Chem. Soc. (London)*, 18, 112, May 7, 1902.

<sup>2</sup> *Am. Chem. J.*, 28, 23.

Weight $\text{La}_2\text{O}_3$ .	Weight $\text{La}_2(\text{SO}_4)_3$ .	Atomic weight.
1.0122	1.7592	138.72
1.1268	1.9581	138.78
0.94585	1.6437	138.77
1.0675	1.8553	138.73
0.9030	1.5692	138.78
1.1273	1.9589	138.79
0.9407	1.6347	138.78
1.0455	1.8168	138.78
1.1271	1.9586	138.78
1.3074	2.2720	138.77
1.3389	2.3267	138.77
1.2012	2.0874	138.78
		Mean, 138.77

An attempt was also made to use the oxalate method, but that proved to be unsatisfactory.

A second memoir upon lanthanum, by Brauner and Pavlicek,<sup>1</sup> is even more elaborate than that of Jones. The method of determination was the same in both cases, but there are many differences of detail. The Bohemian authors find a serious difficulty in the presence of the acid sulphate, for which measured corrections are applied, and they also note another source of error in the hygroscopic character of  $\text{La}_2(\text{SO}_4)_3$ . The latter error was guarded against by special precautions in weighing. The final results (omitting a preliminary series), with vacuum weights, and all corrections applied, are as follows: The calculations depend upon  $\text{O} = 16$  and  $\text{S} = 32.06$ .

Weight $\text{La}_2\text{O}_3$ .	Weight $\text{La}_2(\text{SO}_4)_3$ .	Atomic weight.
1.06562	1.85054	139.036
1.00694	1.74856	139.053
1.12553	1.95457	139.038
1.70276	2.95707	139.026
1.02460	1.77943	139.009
1.28650	2.23419	139.024
1.06488	1.84910	139.068
		Mean, 139.036

The reverse method of determination, the ignition of sulphate to oxide, gave bad results. A series of determinations by the oxalate method gave in mean,  $\text{La} = 139.07$ , but the individual measurements show a wide range of variation, namely, from 138.67 to 139.66. The value for the atomic weight of lanthanum derived

<sup>1</sup> *J. Chem. Soc.*, 81, 1243.

from the sulphate syntheses is doubtless not far from the truth. The mean of the Jones and Brauner values is

$$\text{La} = 139.905,$$

and, pending further evidence, this value may properly be adopted; although Brauner, in a later communication,<sup>1</sup> criticizes the work of Jones and argues in favor of his own determinations. Brauner insists strongly upon the presence of acid sulphate in the lanthanum sulphate studied by Jones, and also suggests that the latter overlooked the hygroscopic nature of his material. If further investigation sustains these criticisms, then the Brauner value is to be preferred.

#### YTTERBIUM.

Atomic weight redetermined by Astrid Cleve,<sup>2</sup> with very pure material. The method employed was the synthesis of the sulphate from the oxide. The data are as follows, when O = 16 and S = 32.06.

Weight $\text{Yb}_2\text{O}_3$ .	Weight $\text{Yb}_2(\text{SO}_4)_3$ .	Atomic weight.
0.7791	1.2535	173.22
0.5190	0.8353	173.05
0.4905	0.7894	173.07

These figures confirm the earlier determination by Nilson.

#### URANIUM.

The work of Richards and Merigold<sup>3</sup> upon the atomic weight of uranium is rich in details, and also in matter relative to probable sources of error. The substance finally chosen for study was uranous bromide prepared by sublimation, and scrupulously protected from the oxidizing action of the air. It contained a minute quantity of sodium bromide, but the amount of this was determined, and the necessary correction was applied. All weights refer to a vacuum, and the antecedent atomic weights were O = 16, Ag = 107.93, and Br = 79.955. A preliminary series of analyses gave as follows, all corrections included:

Weight $\text{UBr}_4$ .	Weight $\text{AgBr}$ .	Atomic weight.
2.2058	2.9699	238.36
1.4418	1.9401	238.69
1.4050	1.8910	238.56
1.1749	1.5818	238.39
		Mean, 238.50

<sup>1</sup> *Ztschr. anorg. Chem.*, 33, 317.

<sup>2</sup> *Ibid.*, 32, 129.

<sup>3</sup> *Proc. Amer. Acad.*, 37, 365.

In another and final set of experiments, the uranous bromide was titrated with known amounts of pure silver, and the precipitated silver bromide was also weighed. Hence two ratios were determined, with the following results:

Weight UBr <sub>4</sub> .	Weight AgBr.	Atomic weight.
1.7999	2.4226	238.54
1.0662	1.4352	238.50
1.8551	2.4967	238.59
		Mean, 238.54
Weight UBr <sub>4</sub> .	Weight Ag.	Atomic weight.
1.7999	1.3918	238.49
1.0662	0.8245	238.46
1.8551	1.4342	238.60
		Mean, 238.52
	Average of all determinations,	238.52
	Average of last six determinations,	238.53

This result is notably lower than the usually accepted value for the atomic weight of uranium.

From series 2 and 3 the ratio between silver and bromine may be deduced. It gives for the percentage of Ag in AgBr the number 57.447. Stas found 57.445. This agreement is eminently satisfactory.

#### RADIUM.

By many fractional crystallizations, Madame Curie<sup>1</sup> has succeeded in preparing radium chloride sufficiently pure for determinations of the atomic weight of the metal. According to Demarcay, who examined the spectrum of the material, it contained a minimum quantity of barium, incapable of exerting any appreciable influence upon the atomic weight. Three analyses were made, the chlorine being weighed as silver chloride, with the following values deduced for the atomic weight of radium.

225.3
225.8
224.0
Mean, 225.0

#### MISCELLANEOUS NOTES.

Several papers have appeared during the year, dealing with numerical relations between the atomic weights of the various

<sup>1</sup> *Compt. Rend.*, 128, 161.

elements. Three of them, by Bilecki,<sup>1</sup> Marshall,<sup>2</sup> and Hollins,<sup>3</sup> relate to possible modifications of "Prout's law"; that is, they point out relations analogous to, but not identical with, those assumed by Prout. Schmidt<sup>4</sup> and Stoney<sup>5</sup> discuss the connection of the atomic weights in a more purely mathematical way, and so too does Vincent.<sup>6</sup> The logarithmic spiral of Stoney is especially suggestive. There is also an elaborate memoir by Lord Kelvin<sup>7</sup> on the "weights of atoms"; and a discussion by Clarke<sup>8</sup> of the best method for the reduction and combination of atomic weight determinations. Ebaugh's work on the atomic weight of arsenic,<sup>9</sup> which was cited in the report of your committee for 1901, has appeared in full in this Journal.

#### INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS.

This committee, which was too large for effective working, has appointed a smaller body for action. This smaller committee, consisting of F. W. Clarke, T. E. Thorpe and Karl Seubert, has already reported, and its report has appeared in this Journal.<sup>10</sup> The table of atomic weights, there given, need not be repeated here.

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## THE DISTRIBUTION OF HYDROGEN SULPHIDE TO LABORATORY CLASSES.

BY CHARLES LATHROP PARSONS.

Received December 2, 1902.

SO MUCH has been written regarding new forms of generators for hydrogen sulphide and their use in the laboratory that one must needs approach the subject with trepidation and, at least, the semblance of an apology. There are, however, few teachers of chemistry who have not experienced the many inconveniences in the use of this most important laboratory reagent, inconveniences that are too frequently little understood by the student himself and which are generally the direct result of wasteful use. It is

<sup>1</sup> *Chem. Ztg.*, 26, 399.

<sup>2</sup> *Ibid.*, 26, 663, and *Chem. News*, 86, 88.

<sup>3</sup> *Chem. News*, 86, 147.

<sup>4</sup> *Ztschr. anorg. Chem.*, 31, 147.

<sup>5</sup> *Phil. Mag.* (6), 4, 411 and 504.

<sup>6</sup> *Ibid.*, (6), 4, 103.

<sup>7</sup> *Ibid.*, (6), 4, 177 and 281.

<sup>8</sup> *Am. Chem. J.*, 27, 321.

<sup>9</sup> This Journal, 24, 489, June, 1902.

<sup>10</sup> V. 28, p. 1, January, 1903; and *Ztschr. angew. Chem.*, 15, 1305.

always easy to instruct students to allow the gas to flow through the solution undergoing analysis at a rate no faster than one or two bubbles a second and always to close the outlet when not in use, but it is an impossibility to attain this result with individuals. Also the constant cleaning and replenishing of the large generators and the limited efficiency which most of them possess has led many instructors to require each student to prepare his own hydrogen sulphide as wanted rather than to depend upon a general laboratory supply. This method is to be deplored even with small classes, while with larger numbers it leads to a laboratory condition which there is no necessity to describe. The constant use in my laboratories, for several years, of the main principle of the apparatus about to be described and the almost complete removal of the difficulties I had before experienced, emboldens me to become a contributor to this already voluminous subject.

#### THE SYSTEM OF SUPPLY.

The usual small lead pipe of approximately 8 mm. diameter is

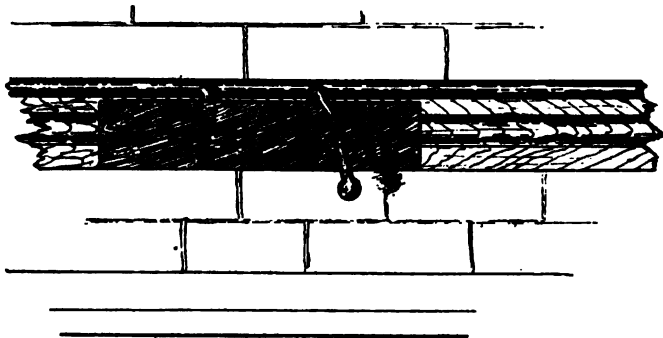


Fig. 1. Detail of outlet.

run from hood to hood where wanted and in each hood any number of short lengths of 4 mm. diameter are soldered on for outlets. The ends of these smaller outlets are then fused together and a fine opening made with a needle. To these lead outlets are attached, by means of a rubber connection, pieces of thermometer tubing bent as shown in Fig. 1 and of such a length that only a limited flow of gas can be obtained under the pressure used. In my own practice, under a pressure of 20 cm., a length of about 12 cm. is required to check the flow down to the rate of 2 bubbles a second which is fast enough for any ordinary use. The ther-



meter tubing is bent as shown in the figure and another short piece of rubber tubing is attached for a final outlet. This is closed with a simple glass plug, which is much to be preferred to a clamp. The whole, with the exception of the end of the rubber tube carrying the plug, is hidden from sight by a wooden block appropriately channeled on the back to receive the thermometer and lead tubing, and screwed on. The student removes the plug, inserts his own delivery tube, secures a fixed flow of gas and, as the whole system is apparently open when he removes his delivery tube, he seldom fails to insert the plug. If he does, but little harm ensues. The flow can be regulated by the length of the thermometer tubing used and the length of tubing required can easily be determined by experiment. A few centimeters variation in pressure makes but little difference in the flow. The rubber tubing connections should be made tight and permanent by slightly heating the lead and glass and they need to be renewed about once each year. There is practically no trouble arising from the stoppage of the capillary tube, only some half dozen tubes having been stopped up in an experience of five years.

#### THE GENERATOR.

The generator (Fig. 2) consists of three essential parts: (1) The acid container *A*. (2) The trap and holder of spent acid *B*. (3) The iron sulphide holder and gas generator proper *C*. All of these parts may be made of glass, porcelain or heavily glazed earthenware. Earthenware is much the cheapest but I have experienced much difficulty in having it made gas-tight. This is fundamental in the construction of the tower and bell *C*. By coating a common earthenware tower with asphalt paint both inside and out I have, however, obtained excellent service from the one now in use.

The acid container *A* holds approximately 10 liters of acid. It is so arranged by means of an inverted jug, or bottle, that the level is maintained constant at *h*. The inverted bottle has a shoulder blown on which, resting on the top of the containing jar, holds it in place. It is filled with 1:8 sulphuric acid or 1:4 hydrochloric acid. The hydrochloric acid is quicker in its action on the iron sulphide and for that reason only is to be preferred. The sulphuric acid, however, is cheaper, answers every purpose and no trouble whatever is experienced from the sulphate formed. The pressure is determined by the perpendicular distance between *h*

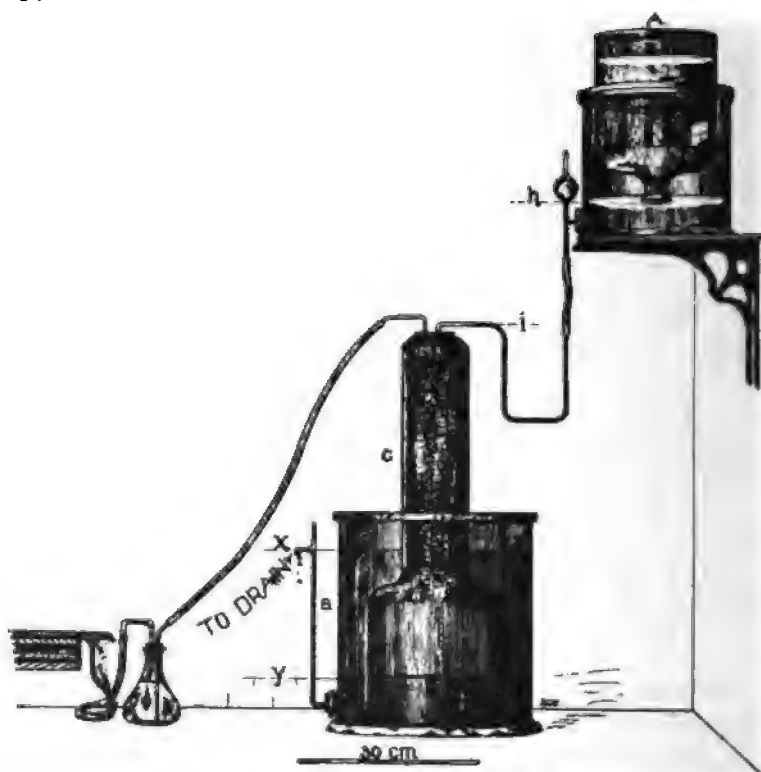


Fig. 2. Generating apparatus.

and  $i$  and is limited by the greatest adjustable distance between the equal and balancing pressure  $x$  and  $y$ . The connection between  $A$  and  $C$  is made by means of a U-shaped glass and rubber tube. It will be easily understood that any increase of pressure in  $C$  caused by the production of gas will immediately force the acid back into the arm nearest to  $C$  thus stopping the flow of acid. The variation due to this increase of pressure, while completely stopping the flow of acid, is seldom so great as a single centimeter, for the enlargement at the bottom of  $C$  takes up the excess of gas and the counterbalancing pressure  $x$  to  $y$  serves as a cushion. The entrance tube at the top of  $C$  should be about 1 cm. in diameter to avoid a slight siphon action which is caused by the short bend where it enters. The glass level outside of  $A$  serves simply to show when the acid supply in the inside container is exhausted, provided this is made of opaque material.

The holder  $B$  is 35 cm. high by 28 cm. inside diameter, and is

provided with a constant level and overflow to drain. It should be covered to prevent evaporation and consequent crystallization of sulphate. The rate of diffusion of a gas through a liquid is so slow that there is practically no odor thrown off into the room from the surface of the liquid.

The tower *C* is the gas generator proper and consists of a bell jar 22 by 25 cm. as a gas holder and pressure cushion, having a few openings at the base for the free passage of liquid. To the top of the bell jar is attached a cylinder 10 cm. inside diameter and 50 cm. high having four constrictions at the base to hold a perforated plate. It is filled with iron sulphide in small lumps or broken sticks. The bell jar and cylinder are best made in one piece, but if made of glass they may be connected by means of a ground joint. This presents no advantage from the standpoint of the chemist but does from that of the glass-blower. The acid enters the tower, drop by drop and in trickling through, the iron sulphide is soon exhausted. Even with a large number of outlets in actual use the acid seldom enters other than dropwise. A small wad of glass wool should be placed on top of the iron sulphide to spread the acid and prevent the formation of channels. The exit tube should pass to a wash-bottle more for the purpose of making the rate of gas flow visible and of detecting any leak in the line when not in use than for any need of purification of the gas. It will also be apparent that when the generator is first placed in action the flow of the acid should be controlled by pressing the rubber tube with thumb and forefinger until the pressure between *x* and *y*, which balances that between *h* and *i*, has established itself.

A generator of this size will easily supply 100 outlets of the form described, even if all were in use at one time. A smaller generator is, however, not to be recommended in any case, for a considerable width and height of the iron sulphide column is essential to its proper working and to insure the almost complete neutralization of the acid. The generator can be easily shut off each night although this is never done in my own practice. A leak is at once made apparent by the gas wash-bottle and easily found with a piece of lead acetate paper.

The following advantages are claimed for this form of generator. They include all of those mentioned by Richards as desir-

able in his very complete article on the subject of gas generators.<sup>1</sup>

(1) Like the Kipp generator it is perfectly automatic so long as the gas flow is choked to less than the maximum capacity of the generator.

(2) The pressure is regulated at will and is almost constant for the height chosen. In practice it seldom varies by so much as a single centimeter.

(3) Only fresh acid comes in contact with the reacting solid.

(4) Under any normal requirements, the full capacity of the acid is obtained.

(5) The products of the reaction are automatically removed. Ferrous sulphate has never, in my experience, crystallized out in the bottom of the apparatus. Some small grains of ferrous sulphate do form in time on the iron sulphide itself but cause no trouble and can easily be removed by running a stream of water through the acid inlet for a few minutes. So far, I have never found this necessary, but it is easily accomplished and may well be done whenever the iron sulphide is renewed. Large crystals do not form.

(6) There are no stop-cocks or valves.

(7) It is easily cleaned and refilled without being taken down, simply by removing a rubber stopper.

(8) When used in connection with the economical choked supply system before outlined, it requires no attention whatever for days or even weeks at a time, depending wholly upon the amount of gas used, and then only to renew the acid, as the iron sulphide will outlast many acid supplies.

(9) If for any reason a large leak develops, the acid runs through rapidly, little iron sulphide is used up, and once the supply of acid has run through all action ceases. Of course, it does not distinguish between a small leak and a legitimate outlet.

The generator works equally well for the production and supply of carbon dioxide, the automatic action being sharper on account of the much more rapid evolution of gas. It is perhaps unnecessary to add that it may be used for the production of hydrogen or for any gas that is set free with a fair degree of rapidity, by the action of a liquid upon a solid.

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<sup>1</sup> *Am. Chem. J.*, 20, 189.

## A PLATINUM CRUCIBLE FOR CARBON COMBUSTIONS.

BY JOHN V. R. STREHMAN.

Received December 13, 1908.

SHIMER<sup>1</sup> has shown that a platinum crucible provided with a special water-cooled stopper and rubber gasket, may be used as successfully as the more expensive platinum tube and gas-consuming furnace for carbon combustions.

The prevalent idea regarding his form of apparatus, seems to be a fear of the rubber gasket causing error by burning directly or by becoming hard and brittle, allowing small pieces to drop into the crucible, when the stopper is pushed into place.

In the following form of apparatus designed by the writer, no rubber gasket or washer is used, and, as in Shimer's apparatus, in place of the furnace, a Bunsen burner or blast-lamp is used, and air in place of oxygen.

It consists, as seen in the drawing, of three parts, *A*, *B* and *C*, also an asbestos washer, *d*. *A* is a water-cooled brass cup. *B* is the cup casing or crucible support, also made of brass. Part *C* is the platinum crucible, provided with a flange around the top, and was remodeled from a 30 cc. crucible. This special shape increases its length and allows over 1 inch to be brought to a full red heat when placed over the burner.

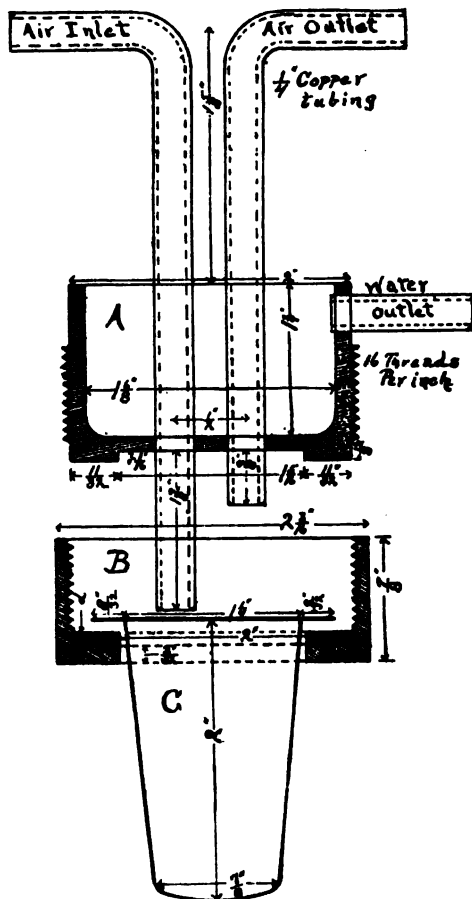
Part *d* is an acid-washed asbestos washer, made from a piece of asbestos wick yarn, of such a length as to allow the beveled ends to lap for about one-half inch. It is moistened and laid in place on the flange of casing *B*, then pressed into place by screwing cup *A* down upon it, the crucible being left out of place. This will force out the excess of moisture in the washer and flatten it. When the washer presents an even surface and has filled the flange of *B* full, it is ready to receive the crucible.

The crucible is now dropped into place, its flange resting upon the washer, and the cup *A* screwed down, using a gentle but firm pressure. That part of the cup *A*, which rests partly upon the flange of the crucible and partly upon the asbestos washer, is turned true, and polished, and coming in contact with the crucible flange and moist asbestos washer insures an air-tight joint. If water is now allowed to circulate through the cup at about 120 cc.

<sup>1</sup> This Journal, 21, 557.

per minute the washer will remain moist when the crucible is heated with the blast-lamp, the casing and cup being protected by the asbestos board.

Two washers may be used, one above and one below the crucible



flange, or the flange of the crucible may rest directly upon the casing flange and the washer placed on top of the crucible flange. The author has used a pure rubber washer, letting it rest directly upon the flange of the crucible, which in turn rested upon the casing flange of B, but it was found that the blank determinations were always high, that is 0.0008 gram, but were constant, if care

was taken not to heat the crucible for more than about five-eighths of an inch from the bottom, to a red heat.

Once in place it is not necessary to remove the crucible, and a large number of determinations can be made, requiring no removal of the crucible, or rearrangement of the washer.

The cup *A*, it will be seen, carries an outlet and an inlet tube for air, brazed into place. It is also provided with an outlet tube for water, and by connecting this tube to a glass tube, giving to the water sufficient fall, it will act as a siphon and carry the water away rapidly. The inflow is obtained by allowing a glass tube attached to some source of supply, preferably the tap, to rest directly upon the bottom of the cup, and having the supply so regulated that the outflow will carry it off.

The train for the combustion of carbon as used with this apparatus consists of the following parts:

(1) Air supply obtained from furnace blast or aspirated from bottles.

(2) Potassium hydroxide bulbs containing potassium hydroxide of 1.40 sp. gr.

(3) A small guard tube to catch any drops of potassium hydroxide that might find their way from the potash bulbs.

(4) Combustion crucible, closed by a special water-cooled cup and casing and resting upon an asbestos board. The bottom part of the crucible projects  $1\frac{1}{4}$  inches through the board and is heated by a flame placed directly beneath it. The whole arrangement is supported by a tripod.

(5) Copper oxide tube; a brass tube 12 inches long and  $\frac{3}{8}$  of an inch in diameter, containing granular copper oxide in that part of the tube which is subjected to redness. This tube is water-jacketed, as recommended by Dr. Sargent.<sup>1</sup> If these water-coolers are made over copper tubes, large enough in diameter to allow the copper oxide tube to slide freely through them, but not too loosely, it will be found a simple matter to replace the copper oxide tube at any time. These coolers are best supplied with water directly from the tap, the outlet of one cooler being connected to the inlet of the other by glass tubing and rubber connections, and the waste water carried to a suitable drain pipe, near at hand. The copper oxide tube rests upon a tripod and over it is

<sup>1</sup> This Journal, 22, 277.

placed a piece of fire-brick, cut so as to form an arch over the tube, and retain the heat. The copper oxide tube is heated for a length of 3 inches to a good red heat, and if the Bunsen flame will not do this, a blast is used allowing it to strike the fire-brick first and curl around the tube.

(6) The next part of the train, is that recommended by Job and Davies,<sup>1</sup> and consists of a U-tube, 6 inch form, containing in the arm nearest the copper oxide tube, thoroughly dehydrated cupric sulphate, and in the other, thoroughly dehydrated cuprous chloride.

(7) A silver sulphate tube containing 10 cc. of silver sulphate solution.

(8) A calcium chloride tube, filled with freshly and thoroughly dehydrated granular calcium chloride.

(9) The potash absorption bulb, same style as used by Dr. Sargent<sup>2</sup> and Job<sup>3</sup> and Davies.

(10) A guard tube of calcium chloride.

The solution of steels is obtained by the use of an acidified solution of double chloride of copper and potassium. The filtration of the carbon is effected as follows. A glass rod, small enough in diameter to pass through the stem of a carbon filtering tube  $\frac{7}{8}$  by 3 inches, is flattened out at one end as recommended by Shimer.<sup>3</sup> Upon this flattened end is supported a platinum perforated disk smaller than  $\frac{7}{8}$  inch, so that it just about clears the sides of the tube when dropped into place. The glass rod and platinum or porcelain disk are put into place in the carbon filtering tube, a layer of dry asbestos previously washed and ignited is made upon the disk, and a little short-fiber asbestos suspended in water is then poured upon it, until a felt of about  $\frac{1}{8}$  inch or more is formed.

The filtering is done upon this bed, using suction. When the washings are completed, the suction is turned on hard and the felt sucked dry. The platinum disk carrying the asbestos felt and carbon residue is then pushed to the top of the funnel tube, and as a general thing it will be found to wipe the sides of the tube free from carbon; when near the top it is pushed forward with a sudden jerk, carrying it out of the tube. It may then be placed upon a watch-glass, put in the oven and dried. The asbestos felt

<sup>1</sup> This Journal, 22, 791.

<sup>2</sup> Loc. cit.

<sup>3</sup> Loc. cit.



and carbon should be transferred from the tube to the watch-glass just as soon as the felt has been freed from excess of water, otherwise the carbon may dry upon the sides of the filtering tube and cannot be wiped clean when the asbestos plug is pushed forward, and this will necessitate the use of a little ignited asbestos to wipe the sides of the tube, the only objection to any form of filtration for carbon which necessitates a transference of the carbon residue.

With such an arrangement 6 or 8 carbons might be filtered at one time, or in the time it generally takes, to filter one, by simply having 6 or 8 tubes suitably connected to a source of suction. With a little practice it will be found that it is not often necessary to clean out the tube with an extra piece of asbestos.

After the carbon plug is dry, it is transferred, carbon side down, to the platinum crucible and it is best, as recommended by Shimer,<sup>1</sup> to have a thin platinum disk in the bottom of the crucible. The platinum disk used for filtering is removed from the asbestos felt before it is introduced into the crucible, a very easy operation as the felt in drying turns up at the edges so that it may be picked up with forceps and transferred to the crucible. The felt carrying the carbon is pressed against the bottom and sides of the crucible, and if it was found necessary to wipe the sides of the filtering tube with ignited asbestos this too is added, keeping it close to the sides of the crucible. If now a platinum disk, the same as used in filtering, is dropped upon the felt it will greatly aid in keeping the heat in the bottom of the crucible, although it is by no means necessary.

The asbestos washer is now moistened with a little water (about 5 or 6 drops), as is also the contact flange of the cup, using the wet finger; the cup is now screwed into place and drawn up tight. The apparatus is placed on the asbestos board, over the tripod, the water connections made, and the air-inlet and air-outlet tubes connected to the absorption train. The copper oxide tube having in the meantime been heating, air is now turned on and allowed to flow at the rate of 4 bubbles per second for five minutes, when the weighed potash bulb is introduced in the train and the Bunsen flame is brought under the combustion crucible;  $\frac{3}{4}$  to 1 inch may easily be brought to a good red heat. The author has been using

<sup>1</sup> *Lec. cit.*

fifteen minutes for a combustion and fifteen for aspiration, with an air flow of 4 bubbles per second during combustion and 5 during aspiration, and combustions may be made in less time than this, as the combustion is completed in from ten to fifteen minutes, and it is simply a matter of washing all the carbon dioxide from the train in as short a time as possible and using the least amount of air.

Blank determinations as obtained with this apparatus do not run over 0.0005 gram, and have been as low as 0.0002 gram. The results obtained on standard samples, the carbon of which was determined by combustion in platinum and porcelain tubes, checked very closely and a series of determinations on the same sample were very concordant.

The following changes might be made in the apparatus: (1) It could be made of aluminum. (2) The upper outside face of both cup and casing might be knurled, affording a better hold in putting together. (3) The cup might be closed and provided with water inlet and the outlet tube connected to the water-jacket of the copper oxide tube, thereby reducing the number of water connections. (4) The air inlet tube should be bent a little towards the center and away from the walls of the crucible. The original cost of the above form of apparatus need not exceed \$5, not of course including the crucible, and can be made in any machine shop.

LABORATORY OF THE E. AND G. BROOKE IRON CO.,  
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## OCCURRENCE OF SALICYLIC ACID IN FRUITS.<sup>1</sup>

BY F. W. TRAPHAGEN AND EDMUND BURKE.

Received November 13, 1902.

FOR the past twelve months or more, tests for salicylic acid in various fresh fruits have been carried on in the laboratory of the Montana Experiment Station with the result of showing its almost constant presence in extremely small quantity.

So far as we know the only similar work has been done by Portes and Desmouliere<sup>2</sup> who report its presence to the extent of

<sup>1</sup> Read at the November meeting of the New York Section of the American Chemical Society.

<sup>2</sup> *J. Pharm. Chim.*, 14, 342.

a milligram to the kilogram of strawberries. Desmouliere, in his doctorate thesis in the Université de Paris, also reports its presence in raspberries, mulberries and licorice root.<sup>1</sup> This, so far as we know, covers all the work done on fresh fruit outside of this laboratory. It is probable that the acid is present as the methyl salt, which is well known in oil of wintergreen, though we have not yet taken steps to prove this.

Among the fruits from which we have obtained the salicylic acid reaction are the following: strawberries, raspberries (both red and black), blackberries, currants, plums, black cherries, apricots, peaches, Concord grapes, crab-apples, standard apples and oranges. In a few instances we have made this work quantitative with the following results:

Currants, 0.57 mg. acid per kilo of fruit.

Cherries, 0.40 mg. acid per kilo of fruit.

Plums, 0.28 mg. acid per kilo of fruit.

Crab-apples, 0.24 mg. acid per kilo of fruit.

Grapes, 0.32 mg. acid per kilo of fruit.

These values, however, are not absolute but only comparative, and represent the amount which we have succeeded in extracting in each case. We distilled the fruit with phosphoric acid, extracted the distillate with ether, took up with a small amount of water, and applied the ferric chloride test after the ether had evaporated. Check analyses made with known amounts of salicylic acid showed that not nearly all of the acid was extracted by this method. We have also found the salicylic acid reaction to be given by tomatoes, cauliflower and string beans.

It seems to us that the bearing of this work is very important, particularly as regards the investigations of food chemists. While these very small quantities may not react to the tests for salicylic acid as usually applied, especially in view of the small amount of material generally worked upon (25 grams), yet a knowledge of its wide distribution may save reporting, on occasions, materials as adulterated to which salicylic acid has not been added. Knowing that salicylic acid may occur in many of the substances, either a quantitative determination will be necessary in each case or it will be well to report only on strong reactions. We were led to this investigation by the protest of a well-known

<sup>1</sup> *J. Pharm. Chim.*, 10, 86.

reputable firm in whose currant jelly we reported salicylic acid but which was present in no greater quantity than we have since found it in the fresh currants. A similar experience was lately had in one of the state laboratories for food control.

In addition to the above work we are studying the distribution of benzoic acid in fruits and vegetables, and hope to be able to publish our results within the year.

MONTANA EXPERIMENT STATION,  
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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY—U. S. DEPARTMENT  
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### IODINE ABSORPTION OF OILS AND FATS.

#### A COMPARISON OF METHODS.

BY L. M. TOLMAN AND L. S. MUNSON.

Received December 22, 1902.

THE Hübl method has been used almost entirely for this determination but it has several faults. First, the solution rapidly loses in strength so that it will change materially during a determination, and after standing a week or so becomes too weak for use. Second, it is so slow in its reaction with some of the oils, such as linseed, that a very serious error is brought about by the change in the strength of the solution during the time of reacting.

Wijs<sup>1</sup> showed how considerable this error might be, and the following table taken from his work shows how much difference the time of titrating the blank makes in the iodine number.

TABLE I.—IODINE NUMBERS OF LINSEED OIL BY HÜBL METHOD.

Time of absorption. Hours.	Blank titrated at beginning.	Blank titrated at end.
2	173.74	.....
7	177.65	170.39
24	181.89	163.16

These figures show a decrease in the iodine number after seven hours, if the blank is titrated at the end of the determination. Wijs considers that the true iodine number in this case lies between 173.7 and 181.89. This variation is a very serious objection

<sup>1</sup> *Chem. Rev. Fett. u. Harzt. Ind.*, 6, 6 (1899).

to the Hübl method, and, on such oils as have a high number, greatly reduces the value of the determination and probably accounts for the wide range of figures obtained by different analysts.

A solution that would remain permanent would completely remove this source of error. Two new solutions have been proposed as substitutes for the Hübl, and it is claimed for both that they change but little with age, and are also more rapid in their action than the Hübl solution, yet give results agreeing very closely with those obtained by the Hübl method.

The Wijs<sup>1</sup> solution is iodine chloride dissolved in glacial acetic acid. The Hanus<sup>2</sup> solution is iodine bromide dissolved in glacial acetic acid. Wijs<sup>3</sup> claims that a solution, made up with acetic acid (99 per cent.) showing no reduction with bichromate and sulphuric acid and containing a very slight excess of iodine in order to prevent the presence of any iodine trichloride, remained practically constant for eighteen months. Twenty-five cc. which were neutralized by 47.3 cc. N/10 thiosulphate at the beginning, at the end required 46.9 cc. N/10 thiosulphate. Lewkowitsch<sup>4</sup> found that after five months the strength of such a solution was practically unchanged. Our experience has been the same. A solution remained practically without change for a month.

Hanus<sup>5</sup> showed that a solution of iodine bromide in glacial acetic acid changes only very slightly in three months, and our experience has corroborated this claim. The Hanus solution was prepared as suggested by Hunt;<sup>6</sup> 13.2 grams iodine were dissolved in 1000 cc. glacial acetic acid (99.5 per cent.), which gave no reduction with bichromate and sulphuric acid, and then enough bromine was added to double the halogen content of the solution. This takes approximately 3 cc. of bromine. The iodine solution should be cold when the bromine is added. Forty cc. of a solution prepared as directed above contained 1.0300 grams of iodine: a month later it contained 1.02791 grams. This difference might easily be due to the difference in temperature at the time the 40 cc. were measured. In order to get strictly accurate results a

<sup>1</sup> *Ber. d. chem. Ges.*, 31, 750 (1898).

<sup>2</sup> *Ztschr. Nahr. u. Genus.*, 4, 913 (1901).

<sup>3</sup> *Ibid.*, 5, 499 (1902).

<sup>4</sup> *Analyst*, 24, 257 (1899).

<sup>5</sup> *Ztschr. Nahr. u. Genus.*, 4, 916 (1901).<sup>1</sup>

<sup>6</sup> *J. Soc. Chem. Ind.*, 21, 454 (1902).

number of 20 cc. portions were measured into stoppered flasks and titrated from day to day. The following table shows that the solution is constant:

TABLE II.

Time of standing. Days.	N/10 thiosulphate = 20 cc. iodine. Cc.
1	45.50
2	45.50
3	45.55
5	45.50
6	45.55
8	45.60

This is enough to show that either of the solutions is satisfactory and very much better than the Hübl in retaining its strength.

The second objection to the Hübl solution is slowness of reaction. The time recommended to be allowed in order to complete the reaction is variously given by different authors from two to twenty-four hours. Allen<sup>1</sup> recommends two hours. The official method of the Association of Official Agricultural Chemists requires three hours. Lewkowitsch<sup>2</sup> recommends four hours. Wijs<sup>3</sup> showed that with linseed oil the absorption was not complete in seven hours and perhaps longer. These different methods will give varying results. Wijs recommends, when his solution is used, fifteen minutes for non-drying fats and oils, thirty minutes for semidrying oils, and one hour for drying oils.

The following table showing results obtained with both Hanus' and Wijs' solutions substantiates these claims.

TABLE III.—TIME NECESSARY FOR COMPLETE ABSORPTION OF IODINE.

Lab. No.	Kind of oil.	Iodine numbers by Hanus' method.			Iodine numbers by Wijs' method.		
		15 min.	30 min.	1 hr.	15 min.	30 min.	1 hr.
773	Cocoonut .....	8.7	8.6	....	....	....	....
22,077	Konut.....	6.4	6.4	....	....	....	....
1,170	Butter .....	35.2	35.4	....	....	....	....
1,168	" .....	35.4	35.5	....	35.8	35.9	36.0
	Oleo oil .....	43.2	43.4	....	....	....	....
4	Oleomargarine.	52.4	51.8	....	....	....	....
5	"	51.9	52.1	....	52.9	....	53.0
9	"	64.6	65.1	....	....	....	....
I	"	52.2	52.4	....	....	....	....

<sup>1</sup> "Commercial Organic Analysis," Vol. II, Part 1, p. 64.

<sup>2</sup> "Chemical Analysis of Oils, Fats and Waxes," 1898, p. 173.

<sup>3</sup> *Chem. Rev. Fett. u. Hariz. Ind.*, 6, 7 (1899).

Lab. No.	Kind of oil.	Iodine numbers by Hanus' method.			Iodine numbers by Wijs' method.		
		15 min.	30 min.	1 hr.	15 min.	30 min.	1 hr.
	Oleomargarine .	80.4	80.5	....	....	....	....
23,606	Lard oil .....	70.0	69.7	....	....	....	....
798	Olive oil .....	90.1	90.4	90.3	90.0	91.2	90.9
960	" " .....	82.1	81.7	82.2	82.6	82.6	82.5
833	" " .....	86.5	86.5	86.5	86.5	86.7	87.2
772	Peanut .....	96.0	97.4	97.7	98.8	99.0	99.0
777	Mustard .....	125.0	126.0	126.0	126.5	126.5	128.0
771	" " .....	....	119.4	120.0	....	118.0	118.2
776	" " .....	....	105.0	105.0	....	104.3	104.6
775	Rape .....	....	107.4	107.5	....	105.8	105.7
770	Corn .....	....	116.8	117.6	117.1	116.1	118.5
774	Poppy .....	136.8	137.4	138.4	138.8	138.9	139.1
1,162	Linseed .....	....	186.3	186.2	183.6	190.2	188.7

For butter, lard, oleomargarine, and olive oil, the reaction is practically complete in fifteen minutes. With cottonseed, sesame, and mustard, thirty minutes are necessary, while with poppy and linseed one hour gives the best results. There seems to be practically no difference between the two solutions in respect to speed of action. Tables IV and V give the results obtained by ourselves on a number of oils by all three methods. Table VI is a compilation of the data available on the three methods.

TABLE IV.—IODINE NUMBERS OF OILS AND FATS.

Lab. No.	Oils.	Häbl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Häbl.	Difference between Hanus and Häbl.
<i>Non-drying.</i>						
	Cocoanut .....	8.93	9.05	8.60	+ 0.12	- 0.33
	Konut .....	6.09	6.43	6.40	+ 0.34	+ 0.31 <sup>1</sup>
1,170	Butter .....	35.3	36.2	35.3	+ 0.90	+ 0.00
1,168	Butter .....	34.8	35.9	35.4	+ 1.10	+ 0.60
	Oleo oil .....	42.6	43.5	43.3	+ 0.90	+ 0.70
1	Oleomargarine	53.6	53.5	52.3	- 0.10	- 1.30
4	" " .....	52.8	53.7	52.2	+ 0.90	- 0.60
5	" " .....	52.5	52.9	52.0	+ 0.40	- 0.50 <sup>1</sup>
9	" " .....	66.3	66.0	64.8	- 0.30	- 1.50
23,606	Lard oil .....	69.3	70.5	69.8	+ 1.20	+ 0.50
487	" " .....	73.7	74.5	73.9	+ 0.70	+ 0.20 <sup>1</sup>
1,181	Magnolia oil ..	81.7	79.4	78.9	- 2.30	- 2.80
1,182	" " ..	76.1	75.6	74.0	- 0.50	- 2.10
772	Peanut " ..	96.3	99.0	97.4	+ 3.00	+ 1.10
1,149	" " ..	94.5	95.2	94.1	+ 0.70	- 0.10
492	" " ..	107.7	109.5	107.7	+ 1.80	+ 0.00 <sup>2</sup>

<sup>1</sup> Commercial oils.

<sup>2</sup> Adulterated with cottonseed.

Lab. No.	Oils.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
770	Mustard oil ..	110.4	118.5	115.5	+ 8.10	+ 5.10
771	" " ..	113.0	118.2	116.8	+ 5.20	+ 3.80
776	" " ..	98.4	104.3	103.8	+ 5.90	+ 5.40
486	" " ..	103.5	112.5	110.2	+ 9.00	+ 6.70 <sup>1</sup>
495	" " ..	106.4	117.3	114.8	+10.90	+ 8.40 <sup>1</sup>
775	Rape oil .....	101.3	105.7	105.2	+ 4.40	+ 3.80
490	" " .....	100.2	104.1	102.8	+ 3.90	+ 2.60 <sup>1</sup>

*Semi-drying and drying.*

	Sunflower .....	106.4	109.2	107.2	+ 2.80	+ 0.80
1,159	Cottonseed oil.	103.8	105.3	105.2	+ 1.50	+ 1.40
1,160	" " ..	106.2	107.3	107.8	+ 1.10	+ 1.60
1,161	" " ..	104.8	106.2	106.7	+ 1.40	+ 1.90
489	Sesame oil ....	106.4	107.0	106.5	+ 0.60	+ 0.10 <sup>1</sup>
444	Corn " ....	119.0	123.2	120.2	+ 4.20	+ 1.20 <sup>1</sup>
491	" " ....	119.0	122.2	119.6	+ 3.00	+ 0.40 <sup>1</sup>
777	" " ....	123.3	129.2	126.0	+ 5.80	+ 2.70
493	Poppy " ....	133.4	135.2	132.9	+ 1.80	- 0.50 <sup>1</sup>
774	" " ....	134.9	139.1	138.4	+ 4.20	+ 3.50
1,162	Linseed " ....	169.8	186.5	184.5	+16.70	+14.70 <sup>1</sup>
1,188	" " ..	179.5 <sup>2</sup>	188.7	183.7	+ 9.20	+ 4.20

It will be seen from these results that for oils and fats with an iodine number under 100 there is little difference between the three methods. For practical purposes they are the same. But this is not so true for the oils with higher iodine numbers. With mustard and rape oil there is a marked difference, 8.4 numbers higher with Hanus's and 10.9 numbers higher with Wijs's method. It is with these oils and linseed oil that there is the widest variation, but there can be little doubt that the higher numbers obtained by the Hanus and Wijs methods are the more correct.

TABLE V.—IODINE NUMBERS OF OLIVE OILS.

Lab. No.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
795	89.7	90.9	90.4	+1.2	+0.7
796	89.7	90.6	90.0	+0.9	+0.3
797	89.8	91.4	90.0	+1.6	+0.2
798	89.7	91.1	90.4	+1.4	+0.7
960	80.9	82.5	81.7	+1.6	+0.8
833	84.8	86.7	86.5	+1.9	+1.7

<sup>1</sup> Commercial oils.<sup>2</sup> Four hours for Hübl determination.



Lab. No.	Hübl's number, 3 hrs.	Wijs's number, 30 min.	Hanus's number, 30 min.	Difference between Wijs and Hübl.	Difference between Hanus and Hübl.
831	85.2	86.7	85.9	+1.5	+0.7
832	84.9	86.5	85.9	+1.6	+1.0
834	84.5	86.1	85.1	+1.6	+0.6
936	81.8	82.8	82.8	+1.0	+1.0
933	80.6	81.6	81.1	+1.0	+0.5
835	82.7	83.1	82.6	+0.4	-0.1
962	81.2	81.5	80.9	+0.3	-0.3
955	82.6	83.6	83.1	+1.0	+0.5
952	81.3	82.2	81.8	+0.9	+0.5
840	86.3	87.8	86.7	+1.5	+0.4
935	80.5	80.9	81.6	+0.4	+1.1
953	79.2	79.9	80.6	+0.7	+1.4
958	81.8	83.1	81.8	+1.3	0.0
959	81.4	83.4	81.9	+2.0	+0.5
954	86.1	87.7	85.3	+1.6	+0.2
934	81.1	82.4	82.3	+1.3	+1.1
956	84.5	85.9	85.6	+1.4	+1.1
932	80.5	82.0	81.4	+1.5	+0.9
961	80.8	82.3	81.1	+1.5	+0.3
836	86.0	87.7	86.6	+1.7	+0.6
931	80.7	82.2	81.5	+1.5	+0.8
838	86.1	87.9	87.1	+1.8	+1.0
839	89.0	91.3	89.9	+2.3	+0.9
837	84.0	...	84.9	...	+0.9
673	83.3	84.1	82.6	+0.8	-0.7
841	86.9	88.0	87.3	+1.1	+0.4
842	87.2	88.1	87.1	+0.9	+0.1
843	85.1	86.6	85.6	+1.5	+0.5
844	84.2	85.0	84.2	+0.8	0.0
1,091	81.9	83.4	82.0	+1.5	+1.10
Average, 36 samples,				+1.2	+0.59

The iodine numbers of the thirty-six samples of olive oils of known purity obtained by the three methods are given in this table. The maximum difference between Wijs and Hübl is 2, the Wijs method always giving higher results. On the thirty-six samples the Wijs method gave an average of 1.2 numbers higher.

The Hanus method gave a maximum of 1.4 numbers higher than Hübl, with an average of 0.59 number higher. This gives the Hanus solution a very slight advantage over the Wijs and this difference seems to hold good on all the oils—the Hanus being slightly nearer the Hübl than is the Wijs.

TABLE VI.—IODINE NUMBERS BY DIFFERENT METHODS.

Variety of oil.	Hübl's number.	Wijs's number.	Hanus's number.	Difference between Hübl and Wijs.	Difference between Hübl and Hanus.	Analyst.
Cocoanut..	9.03	....	9.03	....	0.0	Hanus.
Butter ....	30.7	....	30.6	....	-0.1	"
Lard .....	56.4	....	56.9	....	+0.5	"
Peanut ....	88.3	....	88.4	....	+0.1	"
" ....	87.2	87.2	...	0.0	....	Wijs.
" ....	91.8	93.4	91.6	+1.6	-0.2	Hunt. <sup>2</sup>
Rape.....	99.3	...	98.8	....	-0.5	Hanus.
" .....	102.9	103.3	....	+0.4	....	Wijs. <sup>1</sup>
" .....	103.0	102.1	101.9	-0.9	-1.1	Hunt. <sup>2</sup>
Sunflower .	117.8	119.0	....	+1.2	....	Wijs. <sup>1</sup>
Sesame ...	110.3	111.7	....	+1.7	....	"
" ...	107.1	....	107.5	....	+0.4	Hanus.
Corn.....	124.8	123.4	...	+3.6	....	Wijs. <sup>1</sup>
Poppy ....	122.4	....	122.6	....	+0.2	Hanus.
" ....	134.6	....	135.2	....	+0.6	"
" ....	119.6	119.6	....	0.0	....	Wijs. <sup>1</sup>
Linseed ...	174.8	177.3	174.5	+2.5	-0.3	Hunt. <sup>2</sup>
" ...	180.9	182.1	....	+1.2	....	Wijs. <sup>1</sup>
" ...	170.2	....	171.0	....	+0.8	Hanus.

These figures show practically the same results as the previous tables although not quite so wide a variation, which may be somewhat accounted for by the fact that four hours were used in the Hübl determinations, which gives a little higher figure than the three hours on the higher-absorbing oils. These results show very little choice between the two proposed substitutes for the Hübl method. The Hanus gives results a little closer to the Hübl figures but the difference is of practically no consequence. Its chief advantage over the Wijs is in the ease of preparation. Iodine trichloride is a rather rare reagent and the preparation of the iodine chloride by passing chlorine gas into the acetic acid solution of iodine until the halogen content is doubled is a somewhat tedious operation compared with the addition of bromine. On this account we favor the Hanus solution.

With this change of method, a new set of figures will have to be obtained for the semidrying and drying oils, and such oils as mustard and rape with high iodine absorption. For the butters, lard and olive oil the Hanus method compares satisfactorily with the Hübl. The stability of the solution does not lessen the need

<sup>1</sup> Seven minutes used in determination.

<sup>2</sup> One hour used in determination.

of blanks for each set of determinations. The high coefficient of expansion of glacial acetic acid, 0.00115 for  $1^{\circ}\text{C.}$ , makes an appreciable error if a slight change of temperature takes place, as will be seen from the following table.

TABLE VII.

Temperature. $^{\circ}\text{C.}$	40 cc. iodine monobromide in N/10 thiosulphate.
16.0	92.05
17.5	91.85
18.5	91.80
21.5	91.35
24.5	91.10
27.0	90.80
$11^{\circ}$ change	1.25 cc. decrease.

A change of  $\pm 1^{\circ}\text{C.}$  gives a change of  $\mp 0.11\text{ cc.}$  in the amount of N/10 thiosulphate necessary to neutralize 40 cc. of the iodine solution, so that a blank titration of the iodine solution could easily vary 1 cc. N/10 thiosulphate in a day, which would completely vitiate the results.

## DOES CHOLESTEROL OCCUR IN MAIZE OIL?

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

Received December 31, 1908.

ACCORDING to Hoppe-Seyler<sup>1</sup> and to Hopkins,<sup>2</sup> cholesterol occurs in maize oil. As there is evidence of the occurrence of this substance in no other vegetable oil, except olive oil, this is interesting, and of possible importance as a means of detecting maize oil in mixtures with other oils. The statement of Hoppe-Seyler was made before this group of bodies was clearly differentiated, however, and the melting-point ascribed by Hopkins to the alcohol found by him in maize oil is not the true melting-point of cholesterol. The difference in the melting-points is shown below. Cholesterol,  $146^{\circ}\text{--}147^{\circ}$ ; <sup>3</sup> "cholesterol" from maize oil,  $137^{\circ}\text{--}137.5^{\circ}$ .<sup>3</sup> Hopkins used no other means of identification except the color

<sup>1</sup> *Bull. Soc. Chim* [2], 6, 342 (1866); *Medicin.-chem. Untersuch.*, 1, 162.

<sup>2</sup> *This Journal*, 20, 948 (1898).

<sup>3</sup> Wislicenus and Moldenhauer: *Ann. Chem.* (Liebig), 146, 179 (m. p.  $147^{\circ}$ ); Reinitzer: *Monatsh. Chem.*, 9, 422 (m. p.  $147.5^{\circ}$ ); Hesse: *Ann. Chem.* (Liebig), 192, 177 (1878) (m. p.  $145^{\circ}\text{--}146^{\circ}$ ); Salkowski: *Ztschr. anal. Chem.*, 26, 367 (m. p.  $146^{\circ}$ ); Bömer: *Ztschr. Untersuch. Nahr. u. Genuss.* (1898), p. 81 (average m. p. of fifty-two samples,  $146.4^{\circ}\text{--}147.3^{\circ}$ ).

reactions, which are not reliable. These considerations seemed to offer a field for investigation.

The method employed for isolating the compound was substantially that of Forster and Riechelman,<sup>1</sup> which consists in the extraction of the oil with 95 per cent. alcohol and separation of the substance sought from the saponified alcoholic solution. Four hundred grams of oil were extracted with 300 cc. of alcohol in successive portions of 100 cc. each, the oil being boiled half an hour with each portion in a liter flask provided with a reflux condenser. After cooling, each portion of alcohol was drawn off by a separatory funnel and the combined extracts were saponified by boiling two hours with 40 cc. of alcoholic soda 1:3. The greater part of the alcohol was then distilled and the residue, transferred to an evaporating dish, was carried to dryness on a water-bath. The dried and powdered soap was extracted with three portions of ether of 200 cc. each by shaking in a wide-mouthed stoppered bottle; after settling, the ether was decanted through a filter. The filtered extract was distilled and the residue purified by repeated recrystallization from alcohol.

In applying this method to different portions of oil, it was found that while extraction of the dry soap was tedious and attended by loss of ether and, furthermore, gave a product which was quite impure, the extraction of the aqueous solution of the soap was more rapid, more nearly complete and yielded at once a crystalline residue of a fair degree of purity. For a quantity of oil weighing 600 grams, good results were obtained by dissolving the soap in 250 cc. of water and extracting the solution with ether in 100 cc. portions; after four or five extractions the solution was found practically exhausted. It was found advantageous to distil from the alcoholic extract of the oil a considerable portion of the alcohol before saponification and to use alcoholic potash rather than soda. In this way pure characteristic crystals can be obtained without difficulty from 50 grams of oil.

In working with large quantities of oil, from 500 to 1800 grams, the extraction with alcohol was successfully carried out in an ordinary tin (gallon) can heated on a water-bath. A half-inch brass tube was soldered into the cover and connected by a short piece of stiff rubber tubing with a reflux condenser; the rubber

<sup>1</sup> *Ztschr. für öffentl. Chem.*, 3, 10.

tube was used to permit thorough shaking of the can during extraction. The cover was sealed by winding about it before insertion a string smeared with a dextrin paste.

Altogether about 4 kilos of maize oil were examined according to the method outlined above; based on the extraction of one portion of 600 grams, the yield of fully purified crystals was 0.22 per cent. These melted, when dried at  $100^{\circ}$ , at  $138^{\circ}$ - $138.3^{\circ}$ ; when dried *in vacuo*, at  $137.5^{\circ}$ - $138^{\circ}$ ; and after 18 months, at  $128^{\circ}$ - $130^{\circ}$ . To the naked eye the crystals from alcohol, appeared to be broad needles; under the microscope they were found made up of thin laminae much longer than broad and pointed at the ends.

From Raoult's method of molecular weight determination, results were obtained increasing with the concentration, showing association in benzene, the solvent used.

The acetate was made by boiling for one hour with an excess of acetic anhydride. The product was washed with water and then with hot alcohol. From the ethereal solution crystals were precipitated by alcohol, which, purified by recrystallization and dried at  $100^{\circ}$ , melted sharply at  $127.1^{\circ}$ ; they seemed less soluble in alcohol than the corresponding substance obtained from olive oil.

The propionate was made like the acetate and was purified similarly. When dried at  $100^{\circ}$ , the crystals melted at  $108.4^{\circ}$ ; they were more soluble in alcohol than were those of the acetate.

The benzoate was made by fusion with an excess of benzoic anhydride, the mixture being heated in an open tube to initial boiling. The product was boiled some minutes with alcohol and was then thrown on a filter and washed with boiling alcohol and with small portions of warm ether. The yield was small but there was no attendant discoloration and the crystals seemed pure. On crystallization from ether they formed oblong rectangular plates, often with re-entrant angles. The melting-point was  $142^{\circ}$ - $142.5^{\circ}$ .

The color reactions were as follows. In dilute chloroform solution, sulphuric acid produced a rather bluish pink, while the acid layer was yellow. In concentrated solution, the acid layer was yellow and the chloroform a blood-red which became purple on standing. In dilute acetic anhydride solution, sulphuric acid produced a clear green which, on standing, changed to a pure yellow. In concentrated solution the color was a deep bluish

green, permanent for twenty-four hours. Though these reactions and those of the high-melting alcohols of wool grease are too much alike to be of value in analysis, the following differences were observed. On standing, the chloroform layer of Salkowski's test is blood-red with a concentrated solution of wool grease alcohol, and purple with the alcohol from maize oil. With Lieberman's test, in dilute solution, wool grease alcohol gives a bluish green which becomes reddish yellow on standing, while maize oil gives a clear green changing, on standing, to a yellow free from red.

The above results seem sufficient to prove that the alcohol of maize oil is not cholesterol. As shown by the following comparative table, the compound studied is undoubtedly identical with the compound found in wheat and rye and described by Burian under the name "Sitosterol."<sup>1</sup> It is also probably identical with the "Hydrocarotin" of Reinitzer.<sup>2</sup>

#### MELTING-POINTS OF SITOSTEROL AND ITS ESTERS.

Sitosterol.	From wheat.	From maize oil.	Hydrocarotin.
Sitosterol.....	137.5°	138°	137.4°
" acetate.....	124.5°-127° <sup>3</sup>	127.1°	127.6°
" benzoate...	145.0°-145.5°	142.0°-142.5°	144°
" propionate.	108.5°	108.4°	....

### SITOSTEROL, A POSSIBLE TEST FOR MAIZE OIL.

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

Received December 31, 1902.

WHILE the presence of cottonseed oil in other oils is easily detected, the recognition of adulteration of cottonseed oil itself is less simple. The addition of many oils would be shown by their effect on the usual analytical constants, but with maize oil these values show so little divergence from those of pure cottonseed oil that detection of admixture is difficult. Since, however, maize oil contains sitosterol<sup>4</sup> while cottonseed oil contains phytosterol, it seemed that a test might be based upon this difference.

In the preceding article it was observed that the acetate of sitosterol from maize oil seemed rather less soluble in alcohol than

<sup>1</sup> *Monatsh. Chem.*, 18, 351-374 (1897).

<sup>2</sup> *Ibid.*, 7, 597-608.

<sup>3</sup> Softened at 124.5° and melted at 127°.

<sup>4</sup> See the preceding article.

the acetate prepared from olive oil. It was thought that if a relatively small amount of maize oil were to be mixed with an oil known to contain phytosterol, it would be possible to secure by recrystallization of the acetates a portion whose melting-point would approach that of sitosterol acetate. The following trials were therefore made.

A pure cottonseed oil, a cottonseed oil containing 10 per cent. of maize oil, and one containing 20 per cent. of maize oil were extracted, using 50 gram portions, by boiling twenty minutes at a reflux condenser with 100 cc. of 95 per cent. alcohol. The mixtures were then run into separatories and left over night. The clear alcoholic layer was drawn off, boiled fifteen minutes with 75 cc. of half normal alcoholic potash, evaporated to dryness and the residue dissolved in 40-50 cc. of water. The cooled soap solution was shaken out with 75 cc. of ether and 3 cc. of alcohol, and the extract was washed three times with water and evaporated. The yield by this process, which was not expected to give complete extraction, was as follows: Pure cottonseed oil, 0.095 per cent.; 10 per cent. maize oil, 0.12 per cent.; 20 per cent. maize oil, 0.164 per cent.

The crystals obtained were acetylated without further purification by boiling one hour with an excess of acetic anhydride in a beaker covered with a watch-glass containing a little water. The excess of anhydride was evaporated on the water-bath and the acetates recrystallized from alcohol. In recrystallizing, the acetates were dissolved in hot 95 per cent. alcohol and water was then added drop by drop as long as the solution remained clear after shaking; as soon as there were indications of permanent opalescence a few drops of alcohol were added until the solution was perfectly clear. The beaker was then set aside and the crystals subsequently formed were filtered off, dried at 100° C. and the melting-point determined. Proceeding in this way the melting-points shown on the sixth, and subsequent, crystallization were: Pure cottonseed, 120°-121°; 10 per cent. maize, 121.5°-122.5°; 20 per cent. maize, 124°-125°. By dissolving the acetates in hot 95 per cent. alcohol just sufficient for solution and then chilling, there was obtained from the 20 per cent. oil after four crystallizations a portion which showed the melting-point 126°-127°; the melting-point of the acetate from the 10 per cent. oil was unchanged.

The crystals deposited on slow cooling from 95 per cent. alcohol were, in the case of pure cottonseed, transparent flat needles; the 20 per cent. maize oil gave crystals which beside these needles, showed an opaque, white, and more granular form; the crystals from the 10 per cent. oil resembled those from the pure cottonseed oil.

Portions of the crystals obtained from the dilute alcohol, as described above, were allowed to crystallize from a little 95 per cent. alcohol on glass slides and examined microscopically. All three acetates showed massed crystals in branching coral forms and also long narrow plates resembling the crystals of phytosterol and of sitosterol. There seemed to be less difference in the crystal forms as thus examined than appeared to the naked eye in the manner of growth of the crystals when slowly deposited.

It would seem that the above test will detect the addition of 10 per cent. of an oil containing sitosterol to an oil carrying phytosterol. While maize oil is the only commercial oil in which sitosterol has so far been definitely reported, Bömer and Winter<sup>1</sup> have obtained acetates melting at 128° and above from linseed, rapeseed and sesame oils; it seems probable that sitosterol is present in more oils than has hitherto been supposed and consequently that the test can only be regarded as conclusive evidence of the presence of maize oil when the analytical constants show the absence of other adulterants.

As the melting-point varies with the method employed, it will be advisable for the operator to determine the melting-point of phytosterol acetate according to the method he himself uses. The above values were determined in straight narrow tubes attached to the bulb of an Alverginat thermometer and suspended in a test-tube of sulphuric acid. This was in turn suspended in a 100 cc. flask about two-thirds full of acid. The flask was supported about an inch above an iron plate heated by a small Bunsen flame. The melting-point was approached fairly rapidly and when within 2° or 3°, the rate of heating was reduced to about 0.2° per minute. The value obtained by Bömer and Winter for the phytosterol acetate from cottonseed oil is 123°-124°, but it may be stated that the values obtained by Bömer for the melting-point of phytosterol are rather higher than those usually reported.

<sup>1</sup> *Ztschr. Unter. Nahr. u. Genuss.*, (1898), p. 81.



## ON THE RELATION OF THE SPECIFIC GRAVITY OF URINE TO THE SOLIDS PRESENT.

By J. H. LONG.

Received December 29, 1902.

ATTEMPTS have been made several times to establish a relation between the specific gravity of normal urine and the weight of solids dissolved in the secretion. Such efforts are naturally based on the assumption that while the solids must vary, the variations remain within rather narrow limits and the two most important constituents must change in the same direction. These two important substances are urea and sodium chloride, and the specific gravity observed depends largely on the weight of these bodies present.

From early experiments of Trapp, Haeser and others, repeated later by Neubauer,<sup>1</sup> the relation appeared in general to be definite enough to warrant the use of the so-called coefficient of Haeser in making an approximate estimation of the urine solids from an exact determination of the specific gravity. The direct estimation of solids by evaporation is apparently easy, but unfortunately is liable to an error due to the partial decomposition of urea into ammonium cyanate and that into ammonia and carbonic acid. In addition to this, there is a loss on account of the slightly stable ammonium salts present, which fact is generally overlooked, although its importance is as great as that of the loss from the urea, in some cases. Unless a correction is made for these losses, the error in the final result is rather large, in fact usually larger than is the difference between the true result and that obtained by applying the coefficient of Haeser.

As this is a point of no little importance, I have recently undertaken a new determination of the urinary solids along with the corresponding specific gravities, both determinations being made as accurately as possible. The solid residue was found by the method originally suggested by Neubauer. About 5 grams of urine are evaporated in a porcelain boat which is placed in a horizontal glass tube passing through a steam-bath. The glass tube is connected with a small flask containing standard sulphuric acid in such a manner that a current of dried air may be aspirated through the whole apparatus and carry evolved products into the

<sup>1</sup> *Ztschr. anal. Chem.*, 1, 166.

standard acid. A subsequent titration with standard alkali and methyl orange shows how much acid has been neutralized by ammonia from the evaporated urine. Three to four hours are given to each evaporation, after which the residue in the boat is allowed to stand about two hours over sulphuric acid before weighing. Neubauer suggested to calculate the ammonia absorbed by the dilute standard acid to urea and add this to the weight of the residue. This has been done in the urine evaporations given below, although the method is not strictly correct, as will be pointed out.

The specific gravities were found by means of a small pycnometer and at a temperature maintained at  $25^{\circ}$ , with a variation within  $0.1^{\circ}$ . For possible practical applications,  $25^{\circ}$  is a much more suitable temperature than is  $15^{\circ}$  or even  $20^{\circ}$ . The results are referred to water at  $4^{\circ}$  as unity and are all given below.

Some preliminary experiments were made to determine the loss in evaporating solutions containing pure urea and certain salts in proportions corresponding to those obtaining for urine. In the first of these I took, with water enough to make about 4 cc. :

	(a).	(b).
NaCl .....	0.0930	0.0708
K <sub>2</sub> SO <sub>4</sub> .....	0.0077	0.0059
CON <sub>2</sub> H <sub>4</sub> .....	0.1467	0.1117
	<hr/>	<hr/>
	0.2474	0.1884
Residue recovered.....	0.2430	0.1851
Urea from ammonia .....	0.0052	0.0037
	<hr/>	<hr/>
	0.2482	0.1888

In the first case, the loss of 5.2 mg. of urea calculated from the ammonia is 3.5 per cent. of the urea present or 2.1 per cent. of the solids. In the second case, 3.7 mg. amounts to 3.3 per cent. of the whole urea, or 2 per cent. of the total solids. Very similar results were found in other tests and need not be given in detail. In the following experiments the effect of a phosphate was determined. With water enough to make about 3.5 cc. in each case, I took :

	(c).	(d).
NaCl .....	0.1126	0.0881
K <sub>2</sub> SO <sub>4</sub> .....	0.0080	0.0101
HNa <sub>2</sub> PO <sub>4</sub> .....	0.0120	0.0120
CON <sub>2</sub> H <sub>4</sub> .....	0.1526	0.1927
	<hr/>	<hr/>
	0.2852	0.3029

The evaporation was continued three and a half hours, and the ammonia was caught as before.

Recovered directly .....	0.2830	0.2991
Loss .....	0.0022	0.0038

The ammonia evolved was found in (c) to be equal to 0.5 cc. of N/4 acid and in (d) to 0.6 cc. of N/4 acid. Calculating this as urea would more than account for the loss. In this case, however, a part of the carbonic acid from the urea decomposition is held by the alkali phosphate. In (c) the total loss was 14.4 mg. per gram of urea, or 1.44 per cent. of the total urea. In (d) the loss was 19.2 mg. per gram of urea or 1.92 per cent. of the urea present. These losses are about one-half as great as they were in the absence of the alkali phosphate.

Since the urine is commonly slightly acid and probably from the presence of the dihydrogen phosphate, two further evaporations were made with known amounts of this salt present. It was produced by addition of N/10 sulphuric acid to a solution of the disodium salt. The weights taken, with water enough to make up 4.5 cc., were:

	(c).	(f).
NaCl .....	0.1046	0.1053
K <sub>2</sub> SO <sub>4</sub> ... ..	0.0099	0.0100
Na <sub>2</sub> SO <sub>4</sub> .....	0.0060	0.0060
H <sub>2</sub> NaPO <sub>4</sub> .....	0.0100	0.0100
CON <sub>2</sub> H <sub>4</sub> .....	0.1893	0.1900
	0.3198	0.3213
Recovered directly .....	0.3171	0.3174
Loss .....	0.0028	0.0039
The ammonia evolved calculated as urea gives .....	0.0023	0.0037

In such cases, therefore, it seems perfectly proper to add urea to correct the evaporation loss, and the presence of the salts does not appear to increase this appreciably. The decomposition with alkaline phosphate present is probably the same, but the ammonia only is fully liberated.

Below are given the results of fifty-two determinations on the urine of six persons. The samples taken for the tests did not represent the excretion of the whole day but were chosen to represent extreme cases, as far as possible, as the main object of the

investigation was to determine the limits of variations. From other investigations, the average amounts of urea and ammonia excreted by the same individuals, under the same general conditions, had been determined. The urea amounted to 28 grams per liter and the ammonia to 650 mg. per liter. All the tests were made on perfectly fresh urine, from individuals in normal health, consuming an average meat, vegetable and bread diet.

No.	Sp. gr. $25^{\circ}$ <sub>4</sub>	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
1	1.0199	51.57	2.36	0.259
2	1.0207	51.19	2.95	0.247
3	1.0206	52.33	2.37	0.254
4	1.0189	44.28	2.28	0.234
5	1.0209	53.70	2.14	0.257
6	1.0215	53.10	1.72	0.247
7	1.0227	61.93	2.89	0.272
8	1.0217	53.51	2.46	0.247
9	1.0224	56.54	2.13	0.252
10	1.0180	53.84	2.51	0.299
11	1.0252	66.05	2.56	0.262
12	1.0251	63.54	2.10	0.253
13	1.0226	57.19	1.71	0.253
14	1.0231	60.00	1.95	0.260
15	1.0236	57.38	1.76	0.243
16	1.0236	62.82	2.35	0.266
17	1.0248	59.90	2.74	0.242
18	1.0279	70.73	1.75	0.254
19	1.0230	59.31	1.70	0.258
20	1.0279	75.21	1.96	0.270
21	1.0223	57.48	2.09	0.258
22	1.0177	43.13	1.60	0.244
23	1.0231	63.06	1.92	0.273
24	1.0228	58.37	2.15	0.256
25	1.0284	75.55	1.67	0.266
26	1.0256	73.26	2.34	0.288
27	1.0246	59.75	1.93	0.243
28	1.0191	44.98	2.00	0.235
29	1.0317	79.29	2.31	0.250
30	1.0118	30.02	0.97	0.254
31	1.0237	63.45	4.53	0.268
32	1.0207	51.06	1.73	0.247
33	1.0291	70.90	4.19	0.244
34	1.0243	62.41	2.81	0.257
35	1.0140	37.81	2.01	0.270
36	1.0217	56.56	2.40	0.261
37	1.0225	59.29	2.75	0.264

No.	Sp. gr. <sup>25°</sup> <sub>4</sub>	Solids in grams per liter.	Loss as urea, grams per liter.	Multiplication factor.
38	1.0165	45.13	2.49	0.274
39	1.0212	60.01	3.64	0.283
40	1.0155	43.08	2.91	0.278
41	1.0247	62.74	1.62	0.254
42	1.0113	33.47	2.26	0.296
43	1.0161	44.72	2.03	0.277
44	1.0201	53.46	1.61	0.266
45	1.0231	60.95	2.38	0.264
46	1.0225	55.47	0.98	0.242
47	1.0221	56.19	1.83	0.254
48	1.0120	31.69	1.56	0.264
49	1.0160	41.84	1.60	0.261
50	1.0215	53.98	1.70	0.251
51	1.0267	68.91	1.17	0.258
52	1.0160	41.26	2.12	0.258
Mean,	1.0215	55.83	2.19	0.260

The evaporation losses calculated as urea, from the ammonia evolved, are seen to be far greater with the urine than with the artificial mixtures. With an average of 28 grams of urea in the urine the mean loss is evidently about 8 per cent. of this content. While as a matter of convenience it is satisfactory to calculate the loss as urea, a little consideration will show that a part of it must come from other sources. In the evaporation, part of the ammonia present, and possibly sometimes all of it, is driven off and this may be considered as combined as some organic salt and possibly partly as carbonate. In one case the loss would be less and in the other greater than that found by calculation as urea. The usual method of calculation probably represents the average loss, and this has been included in the figures representing the total solids in column 3.

The correspondence between high specific gravity and high solids is a fairly good one in most cases, as shown by the factor in the last column, representing the so-called Haeser coefficient for the temperature of 25°. This factor is obtained by dividing the last three figures of the specific gravity into the weight of solids found. In most cases the variations are not great from the mean value of 0.260, but in Nos. 4, 10, 26, 28, and 42 the divergence is much greater than given by Neubauer. For the *mixed* day's urine the results would be much closer and in any such case the factor 0.260 would not be far from the truth. This factor can be

applied only when the specific gravity is taken at 25°, for which temperature many urinometers are now adjusted. For an instrument graduated to give the specific gravity at 20° referred to water at 4° the factor to be used is 0.234. This was found by making a number of determinations of the specific gravity at the two temperatures and calculating the average coefficient of expansion. Neubauer's average factor is 0.233, based on urine at 15° referred to water at 0°. For the same temperature limits the results are practically identical, which indicates that for normal mixed urine the coefficient has a sharp definite value, and that it may be used as a control in certain kinds of analyses. Results of still greater value in practice may doubtless be secured through the exact determination of a factor for the solids, exclusive of the sodium chloride, that is, for the products of metabolic origin. A series of determinations in this direction is now in progress.

In any case the *exact* determination of the total solids by evaporation does not appear to be possible because of the uncertainty as to how the ammonia loss should be calculated.

My thanks are due to Mr. C. W. Brown, who made many of the determinations given above.

NORTHWESTERN UNIVERSITY,  
CHICAGO, December, 1902.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE.]

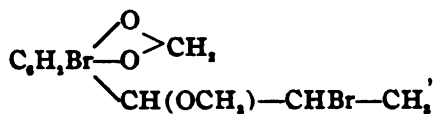
### DERIVATIVES OF ISOSAFROL AND ISOAPIOL.

BY F. J. POND AND C. R. SIEGFRIED.

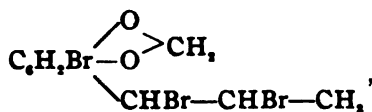
Received January 2, 1903.

IN a previous paper,<sup>1</sup> certain compounds were described which were found to result by the action of hot methyl and ethyl alcohols upon the bromine derivatives of anethol, isosafrol, ethyl isoeugenol and isoapiol; it was stated that these compounds are formed by the replacement of the bromine atom in the side-chain, which stands in the  $\alpha$ -position to the benzene ring, by the methoxyl- and ethoxyl-groups. Thus, for example, a compound having the formula,

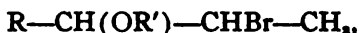
<sup>1</sup> Pond, Erb and Ford : This Journal, 24, 327.



results on boiling monobromisafrol dibromide,



with methyl alcohol. This compound separates from methyl alcohol in large, prismatic crystals, melting at  $75^\circ$  to  $76.5^\circ$ , and it was designated as the methyl alcohol addition-product of dibromisafrol; it may perhaps be better termed  $\alpha$ -methoxy- $\beta$ -brom-dihydro-bromisafrol. The analogous ethyl alcohol product was also described. It was likewise shown that corresponding methyl and ethyl alcohol products are formed in a similar manner from anethol dibromide, monobromanethol dibromide, isosafrol dibromide and ethyl isoeugenol dibromide. The alcohol products resulting from anethol and monobromanethol dibromides, isosafrol and ethyl isoeugenol dibromides, having the general formula,



were found to be readily converted by sodium methylate or alcoholic potash into ketones,



while the compounds obtained from monobromisafrol dibromide are remarkably stable towards alkaline reagents, and they do not yield ketones on treatment with sodium alcoholate. The formation of the ketones from the first class of compounds is due to the elimination of the bromine atom in the  $\beta$ -position as hydrogen bromide, and the resulting unsaturated ether is then converted into a saturated ketone by hydrolysis and subsequent molecular rearrangement. In the second class of compounds, the  $\beta$ -bromine atom is not removed by the ordinary alkaline reagents.

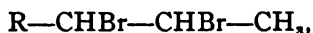
Some months after the completion of the work described in the previous paper, Auwers and Müller<sup>1</sup> published an article on certain derivatives of the bromides of eugenol and isoeugenol. These

<sup>1</sup> Auwers and Müller: *Ber. d. chem. Ges.*, 35, 114.

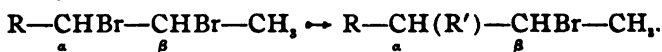
chemists found that the bromine derivatives of eugenol, which may be represented by the general formula,



are not changed by the treatment with alcohols, aqueous acetone, sodium acetate, organic bases, etc., and that they show no abnormal reactions, but possess the character of ordinary phenols. On the other hand, however, the bromides of isoeugenol, having the formula,

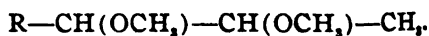
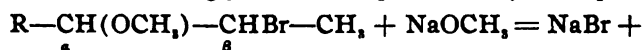


are at once changed by cold methyl or ethyl alcohol, aqueous acetone and sodium acetate, one atom of bromine being eliminated and replaced by the corresponding radical. In every case the bromine atom which is removed is the one standing in the  $\alpha$ -position to the benzene radical; the second or  $\beta$ -bromine atom does not enter into the reaction even at high temperatures or when the reagents, such as sodium acetate, are employed in a large excess. The formation of these compounds is represented by the formulas,



According to Auwers, therefore, the bromides of isoeugenol possess the character of pseudo-phenols, and in general the bromides of para-alkyl phenols, which contain bromine atoms in the  $\alpha$ - and  $\beta$ -positions, react as pseudo-phenols.

A further point of considerable interest in Auwers's work is that when the ethers or alcohols, resulting by the treatment of isoeugenol dibromide or tribromide, are heated with alcoholic sodium methylate, the  $\beta$ -bromine atom is not eliminated as hydrogen bromide, as was found to be the case with the compounds derived from the bromides of isoeugenol ethers investigated in this laboratory, but it is replaced by the methoxyl-group; this reaction gives rise to ethers of glycols as is represented by the equation,

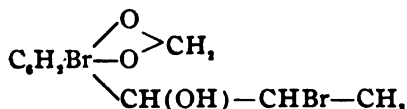


It will be readily seen from the foregoing that Auwers's work is more or less intimately related with the line of investigation which has been conducted in this laboratory for the past three years, the chief difference being that Auwers's researches were carried on with isoeugenol, a compound containing the free phenolic group,

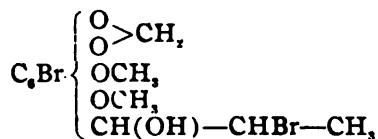


while our work is confined to the ethers of isoeugenol and of other propenyl phenols as anethol, isosafrol and isoapiol. This difference in the constitution of the compounds appears to exert a considerable influence upon the reactions of the substances derived from them, since in no case have we observed the formation of ethers of glycols as described by Auwers.

The experimental work described in this paper is a continuation of our investigations on the action of alcohols and aqueous acetone upon the bromides of isosafrol and isoapiol. From monobromisafrol dibromide we have prepared a new alcohol,



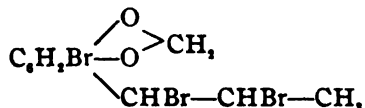
its methyl and ethyl ethers, together with its acetyl and benzoyl derivatives; the same series of compounds is also obtained from monobromisoapiol dibromide, the new alcohol having the formula,



From this alcohol a new ketone has also been obtained.

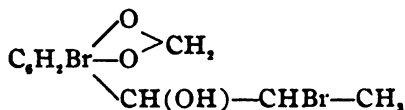
#### EXPERIMENTAL.

##### *Monobromisafrol Dibromide,*<sup>1</sup>



This compound is readily prepared as previously described by treating an ethereal solution of isosafrol with two molecular proportions of bromine. It separates from a mixture of acetone and ether in colorless crystals, melting at 110° to 111°.

##### *α-Oxy-β-brom-dihydro-bromisafrol,*



A solution of 10 grams of monobromisafrol dibromide in 50 cc.

<sup>1</sup> Pond, Erb and Ford: *This Journal*, 24, 340.

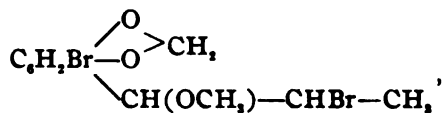
of acetone was heated to boiling and then treated with 15 cc. of water; the aqueous acetone solution was boiled in a reflux apparatus on the water-bath for two hours. The solution at first assumed a red color, which gradually became colorless. On completion of the reaction, the product was poured into an evaporating dish, and, after the evaporation of the acetone, a compound separated as a yellow-colored oil; after standing for about twelve hours, this oil solidified to a white, waxy substance, which was filtered, washed well with water and pressed on a porous plate. The crude compound is exceedingly soluble in alcohol and ether, hence it is best to crystallize first from acetone and to recrystallize from alcohol; it separates from these solvents in beautiful, large crystals, which melt at  $89^{\circ}$ .

Analysis gave the following results: Calculated for  $C_{10}H_{10}O_2Br_2$ , C, 35.50; H, 2.95; Br, 47.33. Found, C, 35.75, 35.78; H, 3.21, 3.07; Br, 47.23.

When this compound is boiled with alcoholic potash or sodium methylate, bromine is eliminated; on acidifying the reaction-product with hydrochloric acid and then adding water, an oil is formed. It was expected that this oil would exhibit the ordinary reactions of a ketone, but it failed to yield an oxime or semicarbazone, and its examination must be continued.

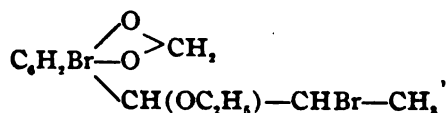
The methyl and ethyl ethers of the foregoing alcohol were described in a previous paper, but they will be briefly reviewed here for sake of completeness.

*$\alpha$ -Methoxy- $\beta$ -brom-dihydro-bromisafrol,*



is formed when a solution of monobromisafrol dibromide in methyl alcohol is boiled for a short time. It crystallizes from methyl alcohol in large prisms, melting at  $75^{\circ}$  to  $76.5^{\circ}$ .

*$\alpha$ -Ethoxy- $\beta$ -brom-dihydro-bromisafrol,*

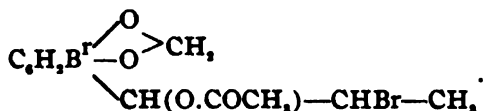


obtained by boiling a solution of isosafrol tribromide in ethyl alco-

hol, crystallizes from alcohol in large crystals, and melts at 58° to 60°.

Boiling, concentrated sodium alcoholate is without action upon these two ethers.

*Acetate of  $\alpha$ -Oxy- $\beta$ -brom-dihydro-bromisafrol,*

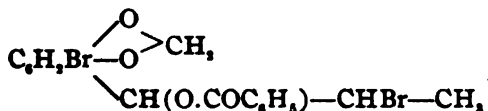


This compound is formed when a solution of 3 grams of potassium acetate in 5 cc. of glacial acetic acid is added to a solution of 10 grams of monobromisafrol dibromide in 15 cc. of glacial acetic acid, and the whole is boiled for about five minutes.

The cold reaction-product is then poured into water; the compound separates as an oil, which solidifies after standing for about twelve hours. It is crystallized from alcohol, dried on a porous plate, and recrystallized from ethyl acetate; it separates from the latter solvent in fine, white needles, which melt at 73° to 74°.

Analysis gave the following results: Calculated for  $\text{C}_{15}\text{H}_{17}\text{O}_4\text{Br}$ , C, 37.89; H, 3.16. Found, C, 37.97, 37.63; H, 3.22, 3.26.

*Benzoate of  $\alpha$ -Oxy- $\beta$ -brom-dihydro-bromisafrol,*

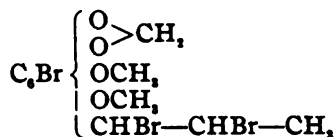


In order to prepare this benzoyl derivative of the alcohol, Einhorn and Hollandt's process was employed, since the ordinary Schotten-Baumann method employs alkali, which would lead to a decomposition of the alcohol.

Five grams of  $\alpha$ -oxy- $\beta$ -brom-dihydro-bromisafrol were dissolved in 15 grams of pyridine, and 3 grams of benzoyl chloride were added slowly, with constant shaking; the mixture was allowed to stand during twenty-four hours, and then poured into dilute sulphuric acid (1:5). The benzoyl derivative separated at first as an oil, but solidified after repeated washing with dilute acid and water, and was crystallized from a mixture of ether and acetone; it forms long, white crystals, melting at 142° to 143°. It is readily soluble in the usual solvents.

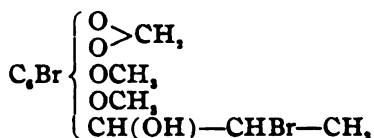
Analysis gave the following results: Calculated for  $C_{17}H_{14}O_4Br_2$ , C, 46.15; H, 3.16. Found, C, 46.27, 46.10; H, 3.24, 3.21.

*Monobromisoapiol Dibromide,*



prepared as previously described<sup>1</sup> by the action of two molecular proportions of bromine upon an ethereal solution of isoapiol, crystallizes from acetone and melts at 120°.

*α-Oxy-β-brom-dihydro-bromisoapiol,*



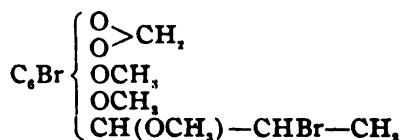
Twenty grams of monobromisoapiol dibromide were dissolved in 100 cc. of acetone and treated with 30 cc. of water; after boiling for two hours in a reflux apparatus, the acetone was allowed to evaporate and the oily residue was washed well with water. The oil gradually solidified, was washed, dried, and crystallized from alcohol; it separated in large, well-defined crystals, melting at 85° to 86°.

The compound is readily soluble in the usual solvents. When boiled with alcoholic potash, one atom of bromine is removed and a new compound is formed, which will be subsequently described.

Analysis gave the figures: Calculated for  $C_{12}H_{14}O_4Br_2$ , C, 36.18; H, 3.52; Br, 40.20. Found, C, 36.21, 35.98; H, 3.61, 3.31; Br, 40.34.

The methyl and ethyl ethers of the above-mentioned alcohol are easily obtained by boiling a solution of isoapiol tribromide in methyl or ethyl alcohol.

*α-Methoxy-β-brom-dihydro-bromisoapiol,*



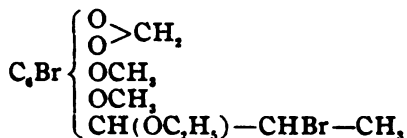
A solution of 20 grams of monobromisoapiol dibromide in 50 cc.

<sup>1</sup> See Pond, Erb and Ford: This Journal, 24, 343.

of methyl alcohol is boiled for a few minutes and then poured into a crystallizing dish; the compound separates in large crystals, which melt at 92° to 93°.

Analysis gave: Calculated for  $C_{13}H_{16}O_5Br_2$ , C, 37.86; H, 3.88; Br, 38.83. Found, C, 38.02, 38.01; H, 3.90, 3.99; Br, 38.78, 38.85.

*α-Ethoxy-β-brom-dihydro-bromisoapiol,*



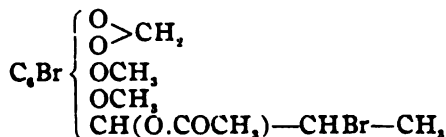
Twenty-eight grams of monobromisoapiol dibromide were dissolved in ethyl alcohol, and the solution was boiled for ten minutes; on cooling, this compound separated in large crystals, melting at 72° to 73°.

In our previous communication, this compound was described as an oil, and at that time it was impossible to induce the substance to solidify; now, however, we find no difficulty in obtaining a crystalline product at once. We are unable to find a satisfactory explanation for this difference in the behavior of the substance, unless we attribute it to a slightly purer isoapiol tribromide.

The compound was analyzed with the following results: Calculated for  $C_{14}H_{18}O_5Br_2$ , C, 39.43; H, 4.22. Found, C, 39.59, 39.20; H, 4.00, 4.05.

Hot, concentrated solutions of alcoholic potash and sodium methylate are without action upon these ethers.

*Acetate of α-Oxy-β-brom-dihydro-bromisoapiol,*



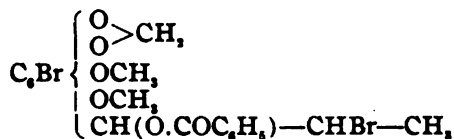
A hot solution of 2.5 grams of potassium acetate in 5 cc. of glacial acetic acid was added slowly, and with shaking, to a warm solution of 10 grams of monobromisoapiol dibromide in 15 cc. of glacial acetic acid, and the mixture was brought to a boiling temperature.

The cold reaction-product was then poured into water, extracted with ether, and the ethereal solution washed with water, dried over calcium chloride, filtered and the ether allowed to evaporate.

The substance remained as an oil, which solidified slowly; it was crystallized from ether and melted at 114° to 115°.

Analysis for carbon and hydrogen gave: Calculated for  $C_{14}H_{16}O_6Br$ , C, 38.18; H, 3.63. Found, C, 37.89, 38.18; H, 3.90, 3.58.

*Benzoate of  $\alpha$ -Oxy- $\beta$ -brom-dihydro-bromisoapiol,*

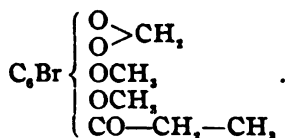


This ester was obtained according to the Einhorn-Hollandt method of preparing benzoyl derivatives.

Five grams of  $\alpha$ -oxy- $\beta$ -brom-dihydro-bromisoapiol were dissolved in 15 cc. of pyridine and treated with 3 grams of benzoyl chloride, which was added gradually. After standing during twenty-four hours, the reaction-mixture was poured into dilute sulphuric acid (1:5), and allowed to remain until the oil, which at first separated, had solidified; the solid was then filtered, washed with dilute acid and water, and crystallized from alcohol. It separates in well-defined crystals, which melt at 117° to 118°.

The following figures were obtained by analysis: Calculated for  $C_{19}H_{18}O_6Br_2$ , C, 45.41; H, 3.58. Found, C, 45.14, 45.13; H, 3.64, 3.44.

*$\alpha$ -Keto-dihydro-bromisoapiol,*



Although the ethers of  $\alpha$ -oxy- $\beta$ -brom-dihydro-bromisoapiol are not affected by boiling with concentrated solutions of alcoholic potash or sodium methylate but, in fact, separate from these solutions on cooling and show their original melting-points, nevertheless the free alcohol itself is quite readily changed by the action of hot alcoholic potash. A similar circumstance was noted in the behavior of the derivatives from isosafrol as described above. The compound obtained from the  $\alpha$ -oxy-isosafrol derivative is an oil, while that formed from the  $\alpha$ -oxy-isoapiol deriv-

ative is a crystalline substance, and analysis seems to indicate that it is a ketone.

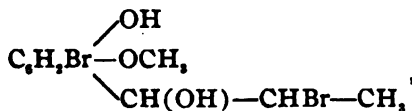
Five grams of  $\alpha$ -oxy- $\beta$ -brom-dihydro-bromisoapiol (m. p.  $85^{\circ}$  to  $86^{\circ}$ ) were dissolved in 25 cc. of ethyl alcohol, treated with a concentrated solution of 2 grams of potassium hydroxide in alcohol, and boiled in a reflux apparatus for about two hours; at the expiration of this time the separation of potassium bromide was complete and 100 cc. of water were added. Five cc. of hydrochloric acid were then introduced, and the whole boiled for about half an hour. After standing for about twelve hours, a solid substance separated; this was filtered, dried, and crystallized from alcohol. It melts at  $128^{\circ}$  to  $129^{\circ}$ .

Another preparation of this substance was made by boiling 23 grams of the  $\alpha$ -oxy-compound with a solution of 7 grams of potassium hydroxide in 100 cc. of alcohol, and subsequently treating with water and acid as above-mentioned. The solid product crystallized from alcohol in beautiful, small crystals, which melt at  $128^{\circ}$  to  $129^{\circ}$  and are rather sparingly soluble in alcohol.

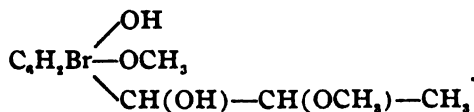
Analysis gave the following results: Calculated for  $C_{11}H_{11}O_2Br$ , C, 45.42; H, 4.10. Found, C, 45.36, 45.67; H, 4.45, 4.31.

The analysis, therefore, indicates the formula given above. That this compound is a ketone, however, has not been absolutely proved, since our investigation was interrupted at this point; we expect to continue it during the current year. It is exceedingly probable that the substance will prove to be the ketone.

According to Auwers and Müller,<sup>1</sup>  $\alpha$ -oxy- $\beta$ -brom-monobrom-dihydro-isoeugenol,

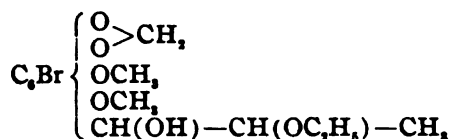


obtained by the action of aqueous acetone upon monobromiso-eugenol dibromide, reacts with sodium methylate, yielding  $\alpha$ -oxy- $\beta$ -methoxy-monobrom-dihydro-isoeugenol,



<sup>1</sup> Auwers and Müller: *Ber. d. chem. Ges.*, 38, 121.

If a similar reaction had taken place in the treatment of  $\alpha$ - $\beta$ -oxy-brom-dihydro-brom-isoapiol with ethyl alcoholic potash, a compound having the following composition would have resulted:



This substance contains 46.28 per cent. of carbon and 5.23 per cent. of hydrogen, which are quite different from the figures obtained by analysis. For the present, therefore, we prefer to retain the ketone formula above-mentioned. This line of investigation will be continued and extended to some other substances of a similar constitution.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE No. 47.—SENT BY H. W. WILEY.]

### THE COMPOSITION OF FRESH AND CANNED PINEAPPLES.

BY L. S. MUNSON AND L. M. TOLMAN.

Received January 2, 1903.

THE work undertaken in connection with the investigation of the composition of fresh and canned pineapples consists of the analysis of (1) fresh pineapples from various sources, (2) canned pineapples that were put up under supervision of the Consuls General of the United States at Singapore and Nassau, and (3) commercial samples of canned pineapples.

#### DESCRIPTION OF SAMPLES.

Of the thirty-eight samples of fresh pineapples examined, twenty-one were from Florida, ten from Cuba, four from Porto Rico, two from the Bahamas and one from Jamaica. The Florida pineapples were largely obtained from representative growers; the Cuban pineapples were nearly all purchased on the market at Havana; the Porto Rican pineapples were obtained from F. D. Gardner, Director of Porto Rican Experiment Station; the Bahama samples were obtained on the market in New York; and the sample from Jamaica was obtained in the Washington market. So far as possible, the samples obtained were the well-ripened fruit, but in some cases they were shipped so far that it was not



practicable to use the thoroughly ripened fruit but such as would stand shipment. Samples 804 to 808 and 818 were secured early in the season and were very green. Their composition shows them to be of inferior quality and therefore they have been excluded from the averages for total solids and for sugars. The first sample of fresh pineapples was received March 4, 1902, and the last sample September 26, 1902, and samples were secured at varying intervals between these dates.

Sixteen samples of canned pineapples were obtained from the Consul-General at Singapore. Of this number, ten were put up in the normal pressed juice of the pineapple without addition of cane-sugar and six were put up in the pressed juice to which cane-sugar had been added. Two samples were obtained from the Consul-General at Nassau, preserved without addition of cane-sugar.

The forty-two samples of commercial canned pineapples came from Singapore, the Straits Settlements and from the Bahamas.

#### METHODS OF ANALYSIS.

The methods of analysis employed in this work were essentially those given under "Fruits and Fruit Products, Provisional Methods for the Analysis of Foods," Bulletin 65, Bureau of Chemistry. The total solids were determined by drying in a water-oven with asbestos for twenty hours. Solids in the syrup were calculated from the specific gravity, using the table of H. Ellion. Reducing sugars were determined by Meissl's method for invert sugar, and cane-sugar was determined both by the increase in reduction after inversion with hydrochloric acid, and by double polarization. The polarimetric method used was that of the German Official Chemists, and cane-sugar was calculated by the Herzfelt formula,

$$S = \frac{100(A - B)}{141.89 + 0.05B - \frac{1}{2}}$$

Results by the two methods agreed very closely, especially where the amount of cane-sugar was small. With samples of high content of cane-sugar, the results by the reduction method were less reliable, owing to the influence of the cane-sugar upon the reduction.

While the acids of pineapples are largely citric they are ex-

pressed in this paper as  $H_2SO_4$  for the reason set forth in a previous contribution from this laboratory.<sup>1</sup>

#### ANALYTICAL DATA.

Table I contains the results of analyses of the fresh pineapples. As will be seen by reference to this table, there is no material difference in composition due to the source of the pineapples; neither does the variety seem to have any influence on the composition. Insoluble solids, ash, acids, and protein do not show a wide variation, while on the other hand the samples show a wide difference in the content of sugars. As is well known, the sugars develop very rapidly with the ripening of the fruit. On the other hand the other constituents appear to be present in equally large amounts in the green fruit. Of particular interest is the relative amounts of reducing- and cane-sugars in the fresh fruit. In nearly all cases the cane-sugar is largely in excess of the reducing sugar. The average amount of reducing sugar in all the samples of fresh fruit is 3.91 per cent. while the average amount of cane-sugar is 7.59 per cent.—nearly double the amount of reducing sugar.

Table II contains the results of the analyses of the pineapples canned under direction of the Consuls General at Singapore and Nassau. The samples put up without addition of cane-sugar were preserved in expressed pineapple juice, the amount of juice added being about 30 per cent. of the entire contents of the can. So far as content of total sugars are concerned, therefore, the composition of these canned pineapples should not be materially different from the composition of the normal fresh fruits. Other constituents, especially insoluble solids, will be lowered by the addition of the juice as comparison of Tables I and II shows. While the amount of total sugar is practically the same as in the fresh fruit, the relative proportions of reducing- and cane-sugars are entirely different, due to the inverting action of the organic acids during the processes of canning. In many cases the amount of the cane-sugar remaining is quite small, the average for all the samples being 3.41 per cent. of cane-sugar and 7.99 per cent. of reducing sugars—just the reverse of the condition in the fresh fruit. This condition also holds in the samples put up with addition of cane-sugar, and with the commercial samples.

<sup>1</sup> This Journal, 23, 347 (1901).

TABLE I.—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids.		Ash.		Acids as H <sub>2</sub> SO <sub>4</sub> . Per cent.	Protein (N X 0.5). Per cent.	Sugar.		Total as Invert.		Polarizations.		Temperature, °C.
		Total. Per cent.	Insoluble. Per cent.	Total. Per cent.	Alkalinity as K <sub>2</sub> CO <sub>3</sub> . Per cent.			Reducing. Per cent.	Cane. Per cent.	Invert. Per cent.	Direct. %.	Invert. %.		
FLORIDA:														
571	Spanish red.....	11.93	1.60	0.438	0.321	0.847	0.406	1.94	5.98	8.24	4.75	—	3.08	22.0
807		8.06 <sup>1</sup>	1.55	0.326	0.390	0.366	0.494	1.74 <sup>1</sup>	2.96 <sup>1</sup>	4.86 <sup>1</sup>	1.85	—	2.20	23.4
808		10.19 <sup>1</sup>	1.59	0.434	0.497	0.825	0.419	1.44 <sup>1</sup>	5.37 <sup>1</sup>	7.09 <sup>1</sup>	4.35	—	2.30	28.4
1054	Spanish red.....	16.53	1.48	0.505	0.377	0.509	0.418	5.89	8.71	15.06	6.70	—	4.45	28.0
1055	Porto Rico.....	12.27	1.48	0.408	0.345	0.307	0.262	4.06	6.49	10.89	5.00	—	3.30	28.0
1056	Egyptian queen..	18.86	1.47	0.548	0.377	0.483	0.381	5.20	8.48	14.13	6.85	—	4.01	28.0
1059	Sugar loaf.....	15.06	1.51	0.356	0.337	....	0.275	3.64	9.12	13.24	8.00	—	3.85	30.0
1060	Spanish red.....	13.30	1.55	0.361	0.243	....	0.474	4.40	6.48	11.22	5.00	—	3.30	30.0
1061	Abakka.....	10.78	1.45	0.385	0.292	....	0.331	3.95	4.68	8.88	3.90	—	2.20	30.0
1062	Blood.....	11.82	1.29	0.446	0.317	....	0.406	3.02	6.13	9.48	5.15	—	2.75	30.0
1063	Spanish red.....	17.52	1.68	0.428	0.374	....	0.418	4.54	10.20	15.28	8.55	—	4.62	30.0
1064	Smooth cayenne.	12.93	1.27	0.378	0.355	0.444	0.400	3.17	7.51	11.08	6.20	—	3.30	27.8
1066	Smooth cayenne.	14.85	1.03	0.373	0.322	0.445	0.393	9.75	2.98	12.89	0.20	—	3.63	27.8
1067	Abakka.....	13.70	1.31	0.349	0.278	0.465	0.419	5.28	6.35	11.97	4.70	—	3.52	27.8
1068	Porto Rico.....	12.20	1.84	0.526	0.478	0.545	0.569	3.98	6.03	10.33	4.60	—	3.08	27.8
1069	Abakka.....	12.73	1.27	0.466	0.418	0.620	0.306	4.38	6.22	10.93	4.80	—	3.30	27.8
1070	Spanish red.....	13.10	1.49	0.464	0.596	0.300	0.475	4.52	6.53	11.40	5.20	—	3.19	27.8
1071	Pernambuco .....	15.60	1.68	0.487	0.403	0.560	0.406	4.33	8.27	13.03	6.50	—	4.23	27.8
1092	Egyptian queen..	13.62	...	0.479	0.459	0.565	0.469	3.62	7.44	11.45	6.40	—	3.08	30.0
1093	Abakka.....	11.02	1.02	0.395	0.276	0.400	0.338	4.08	4.91	9.45	3.40	—	3.02	25.8
1125	Spanish red.....	15.25	...	0.401	0.316	0.560	0.494	4.53	8.22	13.19	6.70	—	4.20	21.0
Average.....		13.85	1.45	0.421	0.370	0.515	0.407	4.44	6.88	11.69				
CUBAN:														
572	Spanish red.....	12.63	1.35	0.272	0.272	0.561	0.406	2.19	6.81	9.36	6.70	—	2.36	21.0
646	Sugar loaf.....	11.45	1.70	0.324	0.355	0.646	0.206	1.76	6.12	8.20	4.80	—	3.19	23.0

<sup>1</sup> Not included in averages.

<sup>1</sup> Not included in averages.

TABLE I (continued).—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids.		Ash.		Acids as H <sub>2</sub> SO <sub>4</sub> Percent.	Protein (N X 6.25) Percent.	Sugars.		Total as invert. Percent.		Polarisations.		Temperature, °C.
		Total.	Insoluble.	Total.	Alkalinity as K <sub>2</sub> CO <sub>3</sub> Percent.			Reducing.	Cane.			Direct.	Invert.	
		Percent.	Percent.	Percent.				Percent.	Percent.			ov.	ov.	
CUBAN:														
647	Spanish red.....	14.12	1.64	0.319	0.328	0.602	0.381	3.00	8.76	12.23	7.10	—	4.33	23.0
802	Spanish red.....	13.45	1.63	0.457	0.461	0.670	0.475	2.31	8.23	10.97	7.20	—	3.57	27.6
803	Sugar loaf.....	12.67	1.80	0.277	0.223	0.502	0.513	2.76	6.77	9.89	5.90	—	3.09	27.6
804		9.13 <sup>1</sup>	1.49	0.313	0.353	0.673	0.512	1.34 <sup>1</sup>	4.60 <sup>1</sup>	6.18 <sup>1</sup>	3.50	—	2.53	23.4
823	Spanish red.....	17.53	1.54	0.425	0.401	0.511	0.387	3.76	10.48	14.79	9.20	—	4.18	28.6
855	Sugar loaf.....	16.53	1.33	0.342	0.360	0.457	0.363	4.55	9.43	14.48	8.10	—	4.29	22.6
860	Spanish red.....	15.38	1.81	0.444	0.476	0.624	0.375	2.84	9.65	12.00	8.35	—	4.07	25.8
1053	Sugar loaf.....	16.99	1.64	0.296	0.327	0.359	0.357	4.65	9.73	14.89	8.50	—	3.90	26.0
	Average.....	14.52	1.59	0.347	0.356	0.561	0.397	3.09	8.44	11.87				
BAHAMAS:														
809		14.97	1.52	0.387	0.410	0.798	0.500	2.56	9.18	12.23	8.10	—	4.07	28.4
868	Spanish red.....	14.65	1.59	0.408	0.409	0.747	0.462	2.75	8.98	12.21	7.85	—	3.74	25.8
	Average.....	14.81	1.56	0.398	0.410	0.772	0.481	2.65	9.08	12.22				
PORTO RICAN:														
805		8.69 <sup>1</sup>	1.64	0.416	0.399	0.697	0.431	1.35 <sup>1</sup>	3.67 <sup>1</sup>	5.22 <sup>1</sup>	2.30	—	2.36	23.4
818	Cabezona .....	8.48 <sup>1</sup>	1.63	0.332	0.304	0.807	0.519	2.74 <sup>1</sup>	3.30 <sup>1</sup>	6.22 <sup>1</sup>	2.30	—	1.92	28.6
819	Pan de Azucar.....	14.14	1.69	0.404	0.437	0.524	0.444	2.97	8.22	11.62	7.15	—	3.41	28.6
820	Caraguena .....	17.69	1.83	0.333	0.370	0.838	0.531	4.59	9.97	15.09	8.20	—	4.62	28.6
	Average.....	15.91	1.70	0.371	0.378	0.716	0.481	3.78	9.09	13.36				
JAMAICA:														
806		9.23 <sup>1</sup>	1.48	0.410	0.410	0.646	0.475	1.28 <sup>1</sup>	4.67 <sup>1</sup>	6.19 <sup>1</sup>	3.55	—	2.58	23.4
	Av'ge of all samples	14.17	1.52	0.396	0.370	0.603	0.420	3.91	7.59	11.90				
	Maximum .....	18.86	1.83	0.548	0.596	0.847	0.569	9.75	10.48	15.28				
	Minimum .....	10.78	1.02	0.272	0.223	0.300	0.206	1.76	2.98	8.20				

<sup>1</sup> Not included in averages.

TABLE II.—COMPOSITION OF CANNED PINEAPPLES PUT UP UNDER DIRECTION OF CONSULS GENERAL AT SINGAPORE AND NASSAU.

Serial Number.	Solids.		Total. Percent.	Ash.		Total. Percent.	Alkalinity as $\text{K}_2\text{CO}_3$ Percent.	Acids as $\text{H}_2\text{SO}_4$ (N X 6.25) Percent.		Sugars.		Total as invert. Percent.	Polarizations.	
	Total. Percent.	Insoluble. Percent.		Reducing. Percent.	Cane. Percent.			Direct. ov.	Invert. ov.	Temperature. °C.				
<i>Preserved in natural juice without addition of cane-sugar.</i>														
SINGAPORE :														
1103	14.34	1.18	0.447	0.312	0.450	0.566	8.92	3.28	12.38	0.90	— 3.30	23.0		
1104	14.26	1.31	0.357	0.295	0.466	0.562	9.54	3.34	13.06	0.90	— 3.52	23.0		
1105	14.41	1.20	0.474	0.338	0.472	0.438	10.96	1.85	12.91	— 1.10	— 3.52	23.0		
1106	13.48	1.15	0.476	0.329	0.490	0.481	9.56	2.44	12.13	0.00	— 3.20	23.0		
1107	17.44	1.44	0.434	0.352	0.436	0.488	10.56	4.11	14.89	1.60	— 3.80	24.4		
1108	13.10	1.34	0.309	0.257	0.450	0.506	7.44	4.20	11.86	2.30	— 3.20	24.4		
1109	10.96	1.16	0.242	0.214	0.250	0.500	5.84	3.85	9.90	2.30	— 2.65	24.4		
1111	11.70	1.62	0.333	0.301	0.333	0.412	7.53	2.08	9.72	0.30	— 2.50	24.4		
1112	11.28	0.87	0.330	0.253	0.294	0.444	6.59	3.00	9.83	1.40	— 2.60	24.4		
1113	12.95	1.83	0.391	0.308	0.299	0.356	7.30	3.17	10.64	1.60	— 2.70	24.4		
Average..	13.39	1.31	0.379	0.300	0.389	0.475	8.42	3.13	11.73					
NASSAU :														
1013	10.00	1.07	0.257	0.300	0.443	0.250	5.44	2.96	8.55	1.65	— 2.09	26.0		
1014	16.35	2.18	0.563	0.663	0.711	0.456	6.20	6.61	13.16	4.65	— 3.68	26.0		
Average..	13.18	1.63	0.410	0.482	0.577	0.403	5.82	4.79	10.86					
<i>Preserved in natural juice with addition of cane-sugar.</i>														
SINGAPORE :														
1114	18.07	1.02	0.370	0.286	0.378	0.412	11.93	4.63	16.70	1.50	— 4.50	24.4		
1115	18.48	1.38	0.267	0.164	0.202	0.350	12.68	4.88	17.82	1.55	— 4.75	24.4		
1116	18.15	1.60	0.460	0.329	0.260	0.400	7.51	8.82	16.80	7.00	— 4.30	24.4		
1117	18.61	2.06	0.505	0.336	0.284	0.456	9.02	7.83	17.26	6.50	— 4.60	24.4		
1118	19.11	1.25	0.450	0.328	0.417	0.450	15.39	2.41	17.93	1.65	— 4.80	24.4		
1119	16.61	1.33	0.334	0.234	0.378	0.375	13.28	2.28	17.93	0.20	— 4.25	24.4		
Average..	18.17	1.44	0.398	0.280	0.320	0.407	11.63	5.14	17.41					



Table III contains the results of analyses of forty-two samples of canned pineapples from Singapore, the Straits Settlements and the Bahamas. It is apparent from the high content of sugars that practically all of the canned pineapples from Singapore and the Straits Settlements are preserved with addition of cane-sugar. On the other hand, the analyses indicate that but few of the samples from the Bahamas have had any addition of cane-sugar.

A study of the data contained in the foregoing tables fails to bear out the common supposition that the pineapples grown upon or near the equator contain more sugar than those grown at some distance farther north, and in fact, the normal content of sugar in pineapples grown in Florida differs so little from that of pineapples grown at Singapore that the difference is practically negligible.

It may not be out of place to state at this point, that these investigations were undertaken in the Bureau of Chemistry at the request of the Secretary of the Treasury for the purpose of establishing a basis of classification for imported pineapples for the guidance of the appraisers. Since the classification of these bodies for dutiable purposes depends upon the answer to the question of whether or not sugar has been added during the process of preserving, it was necessary, first to establish the normal content of sugar in the pineapples. It is evident, from inspection of the analyses, that since the normal pineapples contain a large quantity of cane-sugar, the mere presence of this substance would be no evidence whatever of its artificial addition. It is further evident, that if a syrup containing practically the same quantity of sugar as the natural syrup of the pineapple were added, it would be quite impossible, by a mere determination of the sugar present, to detect the addition. The only guide in this case would be to determine the relation of the sugar present to the total insoluble matters of the pineapple.

If, on the other hand, a syrup rich in sugar were added in preserving, it would be easily detected by the increase in the percentage of sugar in the contents of the can.

In looking over the literature accessible to us relating to the analysis of pineapples, at the commencement of these investigations, we were surprised to find that no paper has been published on this subject except one by Buignet in "*Les Sucres*," published by Maquenne (Paris, 1900).

The average content of sugar found by Buignet, *viz.*, 13.9 per cent. as invert sugar is not materially different from the amount found in these investigations.

## THE EFFECT OF MOISTURE ON THE AVAILABILITY OF DEHYDRATED PHOSPHATE OF ALUMINA.

BY FRED. W. MORSE.

Received January 3, 1903.

THE author has from time to time encountered samples of phosphatic material, which have borne the name of concentrated phosphate, and which really are dehydrated phosphate of alumina and iron.

Such materials usually contain approximately 45 per cent of phosphoric anhydride, of which more than 0.5, and sometimes as much as 0.8, will dissolve in a neutral solution of ammonium citrate.

The phosphatic mineral from which this fertilizer is made, is obtained principally from the islands of Redonda and Grand Connetable in the West Indies, and is a hydrated phosphate of alumina and iron.

The author has made several analyses of the mineral from the former island, and a number of analyses have been published by Shepard,<sup>1</sup> Tate,<sup>2</sup> and Hitchcock,<sup>3</sup> while only one analysis made by Andouard,<sup>4</sup> is yet known to him of the latter phosphate. The composition of the two phosphates is very similar. The phosphoric anhydride ranges from 35 per cent. to 39 per cent. in cargoes and as high as 43 per cent. in the richest specimens.

The water contained in the mineral is nearly proportional to the phosphoric anhydride, the ratio averaging  $2\text{P}_2\text{O}_5$  to  $9\text{H}_2\text{O}$ . Two analyses including Andouard's give  $10\text{H}_2\text{O}$ , while two analyses have been as low as  $8\text{H}_2\text{O}$ . The proportion of  $\text{Al}_2\text{O}_3$  to  $\text{Fe}_2\text{O}_3$  is irregular; usually the former exceeds the latter, especially in the richer specimens.

The process of preparing the mineral for use as a fertilizer, was patented by the late Stephen L. Goodale,<sup>5</sup> who described the prin-

<sup>1</sup> *Am. J. Sci.*, 47, 428.

<sup>2</sup> *J. Soc. Chem. Ind.*, 8, 570.

<sup>3</sup> *Bull. Geol. Soc. Am.*, 2, 6-9.

<sup>4</sup> *Ann. Agronom.*, 21, 171.

<sup>5</sup> "Conversion of Hydrated Phosphates of Alumina and Iron." Monograph, 1893.



ciples of his method in a pamphlet from which the following is quoted.

"The sample properly prepared by reduction to fineness and removal of dust, is gradually heated in a properly equipped receptacle. Elevation of temperature proceeds regularly to about  $100^{\circ}\text{C}$ ., at which point a halt ensues, usually attended by a fall of several degrees. During this halt, heat is apparently absorbed; when the halt ceases, elevation of temperature again proceeds regularly to a point near  $150^{\circ}$ , when another notable halt occurs; when this ceases, elevation proceeds without interruption to full dehydration and beyond, if permitted. This point may be determined by seasonably exposing a cold surface to the orifice where escaping vapor may be deposited as dew. Application of the test should begin at least as soon as  $250^{\circ}$  or  $260^{\circ}$  is reached; the point of complete dehydration varies in samples of differing composition, sometimes as low as  $275^{\circ}$ , rarely beyond  $330^{\circ}$ , usually near  $325^{\circ}\text{C}$ ."

In speaking of the results of the process, Goodale further says: "To attain these fully, the heat must reach the definite, critical point of complete dehydration. If only one-fourth, one-half or three-fourths be expelled, corresponding enhancement in value does not accompany such expulsion. Moreover, if elevation of temperature goes beyond the critical point, change also goes on toward non-solubility, so that most skilful watchfulness is indispensable to avoid loss."

Although this dehydration results in a high percentage of available phosphoric acid as measured by its solubility in ammonium citrate, the use of the calcined phosphate in experiments with plants, has not shown itself to possess any such degree of availability when applied to the soil.

This fact has been especially demonstrated by several series of pot experiments made at the Main Experiment Station,<sup>1</sup> with twelve different kinds of plants; and by three successive years of field experiments at the Rhode Island Experiment Station<sup>2</sup> with a rotation of corn, oats and grass.

It was further noted in the Maine experiments, for which the dehydrated Redonda phosphate was prepared in the Station laboratory, that the availability of the substance in ammonium citrate

<sup>1</sup> Maine Agr. Expt. Sta. Reports (1893), pp. 10-20; (1895), pp. 10-20; (1898), pp. 64-74.

<sup>2</sup> R. I. Agr. Expt. Sta. Reports (1894), pp. 122-128; (1896), pp. 327-343.

decreased on standing, and that it was necessary to prepare a fresh quantity of phosphate for each series of comparisons, which suggested that the dehydrated phosphate reverts to the hydrated condition in the soil. Goodale mentions in his pamphlet that, under certain conditions; the phosphate retrogrades; but does not give any particulars beyond intimating that it is due to over-heating.

In order to get more knowledge of the nature of the dehydrated phosphate, and of its availability, a series of experiments was carried out in the spring of 1900, to determine the amount of dehydration at different temperatures, with the resultant solubility in ammonium citrate of the phosphate, and to see if the dehydrated mineral would revert in the presence of moisture.

In this series of experiments, the author was assisted by Mr. R. H. Shaw, now of the Kansas Experiment Station. For material there was used ground Redonda phosphate obtained in 1891 from Mr. Goodale for field experiments.

The mineral was analyzed with the following results: Water at low red heat, 21.33 per cent.; phosphoric anhydride, 35.92 per cent.

The temperatures selected for dehydration were those mentioned by Goodale, *viz.*, 100°, 150°, 250° and 325° C., and in addition 560° and 830° C., or the fusing points of borax and sodium carbonate respectively.

The estimation of water at 100° was made by heating the mineral in wide weighing bottles, in an air-bath, at a temperature of 100° to 105° C. The material was weighed at intervals of two hours, and the weight at the end of the fourth hour was practically the same as that at the end of the sixth.

At the approximate temperature of 830° the determination was conducted by heating in a platinum crucible over a Bunsen flame, and ascertaining the loss in weight, as in the foregoing experiment. The temperature was reached by adjusting the lamp flame so that anhydrous sodium carbonate was brought to a quiet fusion in a platinum crucible. Then, without disturbing the lamp, the sodium carbonate crucible was removed and another platinum crucible of the same size containing the phosphate was placed in the triangle.

At the intermediate temperatures, the water was not only determined by the loss in weight of the material, but also by the gain

in weight of a calcium chloride tube into which the vapor was passed.

The apparatus was arranged similarly to that for a combustion in a current of air or oxygen, and consisted of a combustion tube connected at one end with a drying tower and at the other end with a weighed U-tube containing calcium chloride.

The charge of phosphate was placed in a porcelain boat, inserted in the combustion tube, and pushed to the middle. For the temperatures of  $150^{\circ}$ ,  $250^{\circ}$ , and  $325^{\circ}$ , a tube oven was used instead of a combustion furnace. For that at  $560^{\circ}$  a special furnace was constructed of a piece of magnesium-asbestos steam-pipe covering, a little shorter than the combustion tube. A rectangular opening was cut in the middle of the lower half-section long enough to admit the tops of three Bunsen burners placed in a line. The tube was supported above the burners by a strip of asbestos board, and when the upper half section was in place, the flames played around the tube as in a combustion furnace. In order to determine the degree of heat sustained by the mineral, a porcelain boat containing anhydrous borax was inserted in the combustion tube along with the boat containing the phosphate, the latter being next to the calcium chloride tube. The borax was maintained at the stage of fusion, which could be observed by removing the upper half section of the improvised furnace.

Determinations of the loss in weight at the temperature of fusing borax were also made by heating in a platinum crucible in exactly the way used with sodium carbonate.

In the tube oven, the temperatures of  $150^{\circ}$  and  $250^{\circ}$  were determined by thermometers as in heating sealed tubes; but since in this operation, a current of air was slowly drawn through the tube, the temperature of the mineral would be somewhat below that registered by the thermometers, which were therefore allowed to run about  $10^{\circ}$  above the stated temperatures before readjusting the lamps.

For the approximate temperature of  $325^{\circ}$ , the thermometer registered  $350^{\circ}$ ; but powdered potassium nitrate contained in a boat placed in the tube reached only the stage of incipient fusion.

The three salts used for determining temperatures were of Kahlbaum's sealed brand of C. P. chemicals, and showed no impurities excepting with the spectroscope.

Richards<sup>1</sup> gives them the following melting-points: Potassium nitrate, 339° C.; sodium biborate, 561° C.; sodium carbonate, 830° C.

In the tube method, at the temperatures of 325° and 560° the water was expelled from the mineral quickly and condensed around the end of the combustion tube next the calcium chloride tube, requiring several hours for its removal by the current of air drawn through the apparatus, since it was necessary to pass the air slowly in order to insure complete absorption.

For the absorption method, it was found necessary to use smaller charges than for the methods depending solely on loss of weight. The effectiveness of the drying-tower was demonstrated by blank determinations, and that of the U-tube by connecting a second calcium chloride tube and weighing it separately. The results are given in the following table.

PERCENTAGES OF WATER EXPELLED AT DIFFERENT TEMPERATURES.

Temperature. °C.	Per cent. by loss.	Per cent. by absorption.
100	18.14	....
150	19.72	19.93
250	20.32	20.26
325	20.71	20.78
560	21.34	20.98
560	21.32	after heating 15 min. in crucible.
830	21.57	" " 5 " " "
830	21.54	" " 15 " " "
830	21.63	" " 30 " " "
830	21.45	" " 60 " " "

The results corroborate the statements of Goodale regarding the expulsion of water at 100° and 150° but do not show complete dehydration at 325°.

The slightly lower results obtained by absorption at 560° were probably due to incomplete removal of water from the combustion tube; but might also be due to the destruction of organic matter which can hardly fail to be present, owing to the fact that the porous phosphate is more or less penetrated by the roots of grasses and cacti, and Andouard in his analysis of Grand Connetable phosphate reports traces of carbon dioxide.

In determining the availability of the phosphate, the official neutral solution of ammonium citrate<sup>2</sup> was used; but the citrate-

<sup>1</sup> *Am. Chem. J.*, 20, 704.

<sup>2</sup> "Methods of Analysis, Association of Official Agricultural Chemists," Bull. 46, Bur. of Chem., U. S. Dept. Agr., p. 11.

soluble phosphoric acid was determined directly, instead of indirectly as in the official method. This was done because in all previous work with this particular phosphate, it was found impossible to prevent the finest particles of mineral running through any paper filter that would permit a ready passage of the citrate solution. Ross' method<sup>1</sup> was therefore selected, which is based on digesting the filtrate of citrate-soluble phosphoric acid with sulphuric acid and oxidizing agents, as in the Kjeldahl method for nitrogen, after which the molybdate solution is used as usual. Of course, this method gives somewhat lower results than the indirect method; but this is not due to incomplete recovery of the phosphoric acid, which was repeatedly verified. The method of procedure then, was to digest 1 gram of the mineral in 100 cc. of neutral ammonium citrate, filter through an asbestos felt with the aid of a pump, digest aliquot parts of the filtered solution after Ross' method, and determine the phosphoric acid as usual. By the use of an asbestos felt, it was possible to get a clear filtrate and to remove the citrate solution quickly from the mineral. The availability of the phosphate at the different stages of dehydration was found to be as follows:

Undehydrated	2.08 per cent. $P_2O_5$
Heated to 100°	19.64 " " "
" " 150°	27.25 " " "
" " 250°	32.76 " " "
" " 325°	31.53 " " "
" " 560°	32.65 " " "
" " 830° 15'	11.35 " " "
" " 830° 90'	2.53 " " "

These results show, that to get the highest degree of availability, it is necessary to remove practically all of the water; but they do not confirm the statement that a continuation of the heat beyond 325° lowers the solubility, since at 560° the mineral underwent the heating for from six to eight hours while the water was being aspirated from the tube. The high temperature required to fuse sodium carbonate produces, however, a marked decrease in solubility, and this is intensified by prolonging the heating.

The effect of exposure to a moist atmosphere was determined by placing the dehydrated phosphate under a bell-jar, in an atmosphere saturated with moisture from an open dish containing water. The phosphate was weighed in a porcelain boat placed

<sup>1</sup> Bull. 38, Bur. of Chem., U. S. Dept. Agr., p. 16.

inside a weighing-tube, and the boat was exposed under the bell-jar, until it had reached equilibrium with respect to moisture, before the dehydrated mineral was weighed into it. The charges used were small, in order to expose as much surface as possible to the action of the moist atmosphere.

The different degrees of dehydration, which were compared, were those obtained by heating to 250°, 325°, 560°, and 830° respectively. The results obtained were unlooked for and of much interest.

Phosphate dehydrated at 250°; charge, 0.2965 gram.

Water absorbed in	24 hours,	0.0565 gram.
" " "	72 "	0.0690 "
" " "	120 "	0.0705 "

Total water absorbed, 23.78 per cent. of charge taken

Phosphate dehydrated at 325°; charge, 0.2200 gram.

Water absorbed in	24 hours,	0.0425 gram.
" " "	72 "	0.0485 "
" " "	120 "	0.0495 "

Total water absorbed, 22.50 per cent. of charge taken.

Phosphate dehydrated at 560°; charge, 0.6495 gram.

Water absorbed in	24 hours,	0.0415 gram.
" " "	48 "	0.0585 "
" " "	96 "	0.0605 "

Total water absorbed, 9.32 per cent. of charge taken.

Phosphate dehydrated by heating fifteen minutes at 830°; charge, 0.4730 gram.

Water absorbed in	24 hours,	0.0065 gram.
" " "	48 "	0.0095 "

Total water absorbed, 2.00 per cent. of charge taken.

The moistened phosphate was next transferred to an ammonium citrate solution and its availability determined by the same method that was employed after dehydration. As the charges of phosphate of the temperatures 250° and 325° were so small, they were combined for the determination of available acid. The quantity of citrate solution was reduced to 50 cc. in all these cases, since the charges were approximately only 0.5 gram each.

The availability of the four grades of phosphate was now found to be as follows:

250° and 325°	19.30	per cent. $P_2O_5$ in dehydrated phosphate.
560°	29.76	" " " " " "
830°	7.09	" " " " " "

The experiment was repeated with the phosphates dehydrated at 325° and 560°.

Phosphate dehydrated at 325°; charges (a), 0.4160 gram; (b), 0.5330 gram.

Water absorbed in 75 hours, (a) 0.0900 gram; (b) 0.1140 gram.

" " " 96 " " 0.0950 " " 0.1200 "

" " " 240 " " 0.1090 " " 0.1460 "

Total water absorbed, (a), 26.20 per cent.; (b), 27.39 per cent. of charge taken.

Phosphate dehydrated at 560°; charges (a), 0.4450 gram; (b), 0.6820.

Water absorbed in 24 hours, (a), 0.0370 gram; (b), 0.0540 gram.

" " " 48 " " 0.0480 " " 0.0660 "

" " " 120 " " 0.0580 " " 0.0800 "

" " " 240 " " 0.0710 " " weight lost.

Total water absorbed in 120 hours, (a), 13.04 per cent.; (b), 11.72 per cent.  
Absorbed in 240 hours, (a), 15.95 per cent.

For the estimation of available phosphoric acid the duplicate charges of each grade were combined, making an approximate charge of 1 gram for each grade, and 100 cc. of citrate solution were used. The availability in this trial was respectively:

325° 11.54 per cent.  $P_2O_5$  in dehydrated phosphate.

560° 27.70 " " " " " "

Having on hand about 200 pounds of the dehydrated phosphate obtained in 1891, which had been stored, since then, in the basement of the laboratory exposed in an open barrel, it was tested for availability in ammonium citrate in order to determine its keeping qualities. In 1891 this lot contained 46.85 per cent. total and 21.91 per cent. available phosphoric acid, and but a trace of moisture. In 1900 a new analysis yielded 10.98 per cent. water; 41.95 per cent. total phosphoric acid and 14.60 per cent. available. The decrease in total phosphoric acid is proportional to the absorption of water, while the drop in available is far in excess of such hydration.

Some of the material was next exposed to a moist atmosphere for eight days, in which time it gained 9.42 per cent. of its weight, and on determining the available phosphoric acid, it was found to have fallen to 11.31 per cent. of the original charge.

The phosphates dehydrated at 325° and 560°, respectively, were next subjected to the action of water saturated with carbon di-

oxide, and its effect was also tried on the undehydrated mineral. One gram of material was taken in each instance and placed in a flask with 200 cc. of water. Carbon dioxide was passed into the water in each flask, during thirty to sixty minutes, twice a day for six days, and the flask was shaken two or three times during its passage. The gas was prepared from sodium bicarbonate and sulphuric acid, to avoid any acid vapors, and was washed before it entered the flask. At the end of the period, an aliquot part of clear liquid was taken from each flask and tested for phosphoric acid. The amount appeared so slight in each case, that no attempt was made to determine the proportion for each grade of material; but the filtrates from the three were combined and then concentrated by evaporation, after which the phosphoric acid was determined as the average for the lot, and found to be 0.31 per cent. of the charges taken.

Each residue was next digested with the ammonium citrate solution and the amount of available phosphoric acid estimated, which was as follows:

Undehydrated		0.69	per cent.	of charge	taken.
Dehydrated at 325°	6.67	"	"	"	"
"	"	560°	24.95	"	"

By these different series of experiments, the rapid deterioration of the dehydrated phosphate with respect to its available phosphoric acid, is clearly shown in the case of the material prepared according to Goodale's process, and the claim is contradicted that heating beyond 325° is injurious. The results show without exception that the temperature at which borax fuses is not too high for good results, and that the phosphate, after being heated to that point, is more permanently soluble, and less apt to again become hydrated. Whether it would be more available to plants than those lots subjected to lower temperatures, cannot be told without vegetation tests.



**NORMAL HEPTYL THIOCYANATE AND SOME NEW ALKYL  
ESTERS OF DITHIOCARBAMIC ACID.**

BY MARSTON TAYLOR BOBERT.

Received January 7, 1903.

SEVERAL years ago, in connection with certain investigations then under way, the writer had occasion to prepare the substances described in this paper. As there is but little likelihood of this line of work being resumed, it seems advisable to record the properties of these new compounds for the information of other workers in this field, particularly since J. v. Braun, in his recent article on the dithiourethanes,<sup>1</sup> calls attention to the fact that only two (ethyl and isopropyl) alkyl esters of unsubstituted dithiocarbamic acid are mentioned in the literature.

*Normal Heptyl Thiocyanate*,  $C_7H_{15}SCN$ .—Normal heptyl bromide was prepared by the action of bromine and amorphous phosphorus upon normal heptyl alcohol, the bromide being driven out of the crude reaction product by a rapid current of steam. The separated bromide was washed with water, with sodium carbonate solution, with water again, dried with calcium chloride, treated with cold concentrated sulphuric acid to remove unchanged heptyl alcohol, washed, dried again and distilled. As thus prepared, normal heptyl bromide forms a colorless oil, boiling at  $175.5^\circ$ – $177.5^\circ$  (uncorr.) at 765 mm., and volatile with steam. In concentrated alcoholic solution this bromide rapidly transposes with potassium thiocyanate, the reaction being complete in about half an hour, if conducted at the boiling-point of the solution. The separated thiocyanate, washed and dried, distils at  $234^\circ$ – $236^\circ$  (uncorr.). Rectified under diminished pressure, the pure substance is obtained as a colorless mobile oil of peculiar but not unpleasant odor, boiling-point  $136^\circ$  (corr.) at 28 mm.; sp. gr. at  $20^\circ$ , 0.92.

*Normal Heptyl Sulphonic Acid*,  $C_7H_{15}SO_3H$ .—The thiocyanate was oxidized by heating with moderately strong nitric acid. After the evaporation of the nitric acid, the syrupy residue was taken up with water, excess of barium carbonate added, the mixture boiled, and filtered hot. The barium salt of the sulphonic acid crystallized from the filtrate, on cooling, in pearly white scales, only moder-

<sup>1</sup> *Ber. d. chem. Ges.*, 35, 3369 (1902).

ately soluble in cold water or in cold 95 per cent. alcohol, and containing no water of crystallization. Spring and Winssinger,<sup>1</sup> by the action of chlorine upon the normal heptyl sulphoxide, obtained a mixture which they believed contained barium heptyl sulphonate, but they did not separate the mixture or obtain the barium salt in question in a pure state.

*Normal Heptyl Dithiocarbamate*,  $H_2NCSSC_7H_{15}$ .—Normal heptyl thiocyanate was treated with hydrogen sulphide at  $100^\circ$ , the hydrogen sulphide being driven in against a pressure of 7 inches of mercury. In the course of six to ten hours, glassy prisms of the dithiocarbamic ester separated. Recrystallized from a mixture of naphtha and carbon bisulphide, large glassy prisms of soapy feel were obtained, melting at  $65^\circ$ , and easily soluble in methyl alcohol, chloroform, benzene, acetone and carbon bisulphide, difficultly soluble in naphtha or kerosene.

*Normal Propyl Dithiocarbamate*,  $H_2NCSSC_3H_7$ , prepared from normal propyl thiocyanate and hydrogen sulphide in a similar manner, crystallizes from a mixture of naphtha and carbon bisulphide, in large colorless prisms, melting-point  $57^\circ$ , insoluble in water, very easily soluble in methyl, ethyl or isoamyl alcohols, in benzene, toluene, acetone, chloroform or carbon bisulphide, easily soluble in hot naphtha or kerosene but on cooling tends to separate as an oil. Through the kindness of Dr. Austin F. Rogers, of the Mineralogical Department of this University, the crystals were measured, with the following results:

Crystals—tabular, parallel to basal pinacoid.

Monoclinic— $a : b : c = 0.8536 : 1 : 0.9447$ .  $\beta = 77^\circ 7'$ .

Observed forms— $c$  (001),  $a$  (100),  $m$  (110),  $t$  (012),  $q$  (011).

		Measured.	Calculated.
$mm'''$	(110 $\wedge$ 110) (7)	$100^\circ 28'$	.....
$cm$	(001 $\wedge$ 110) (6)	$80^\circ 8'$	.....
$cq$	(001 $\wedge$ 011) (6)	$43^\circ 38.5'$	.....
$c'm$	(001 $\wedge$ 110) (3)	$99^\circ 53.5'$	$99^\circ 52'$
$qq'''$	(011 $\wedge$ 011) (4)	$94^\circ 44'$	$94^\circ 43'$
$ct$	(011 $\wedge$ 012) (3)	$24^\circ 45'$	$24^\circ 43'$

Cleavage—perfect, parallel to  $c$ ; imperfect, fibrous parallel to  $a$ .

*Isoamyl Dithiocarbamate*,  $H_2NCSSC_5H_{11}$ , from amyl thiocyanate and hydrogen sulphide, under similar conditions, crystallizes from a mixture of carbon bisulphide and naphtha in glassy

<sup>1</sup> *Bull. Soc. Chim.*, 49, 72.

micaceous scales, melting-point  $51.5^{\circ}$ , easily soluble in methyl or ethyl alcohols, in chloroform, carbon bisulphide, benzene, acetone, very difficultly soluble in boiling water, difficultly soluble in cold naphtha or kerosene but easily soluble in these solvents when boiling.

NOTE.—Since writing the above, an article has appeared by Delépine,<sup>1</sup> in which he describes the methyl, ethyl, normal and isopropyl, benzyl and *p*-nitrobenzyl dithiocarbamates, and gives the melting-point of the normal propyl compound as  $58^{\circ}$ .

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## THE FREEZING-POINTS OF DILUTE SOLUTIONS.

BY THEODORE WILLIAM RICHARDS.

Received January 9, 1903.

THE difficulties which attend the accurate determination of the freezing-points of dilute solutions, according to the ordinary method of procedure, are well known. A brief perusal of the work of Jones,<sup>2</sup> Loomis,<sup>3</sup> Nernst and Abegg,<sup>4</sup> and Raoult<sup>5</sup> is enough to convince even a hasty reader that besides the common errors of thermometry, and of quantitative work in general, the process is especially complicated by the slowness with which the equilibrium is attained. This complication results in either supercooling or superheating, according as the system is being cooled or warmed. Nernst and Abegg performed a valuable service in calling attention to this danger, and the latter of the two, as well as Loomis and Raoult, carried out a few accurate determinations guarding especially against it. Unfortunately, however, their precautions were so elaborate that few experiments were made, and the difficulty seems to have deterred other workers in the same field.

It is easy to see that another method may be used, a method which overcomes the chief difficulty in a simpler manner; and the

<sup>1</sup> *Bull. Soc. Chim.*, 3, 29-30, 48 (1903).

<sup>2</sup> Jones: *Ztschr. phys. Chem.*, 11, 110 and 529; 12, 623 (1893).

<sup>3</sup> Loomis: *Wied. Ann.*, 81, 500 (1894); also *Ztschr. phys. Chem.*, 32, 578 (1900); 37, 407 (1901).

<sup>4</sup> Nernst and Abegg: *Ztschr. phys. Chem.*, 18, 681 (1894); also Abegg: *Ibid.*, 20, 207 (1896).

<sup>5</sup> Raoult: *Compt. Rend.*, 128, 751 (1897).

present paper has as its object the brief presentation of this simpler method.

As has been said, the prime difficulty is the delay in attaining the true equilibrium. Since this equilibrium is one between two phases, it can be adjusted only on the surface between the two. The speed is therefore proportional to the extent of surface. In order then to avoid the danger of superheating or supercooling, one must have as much ice present as possible, instead of as little as possible. Nothing could be easier than the carrying out of the process under these new conditions. It is true that the solution surrounding the ice must be analyzed, but this may often be done volumetrically or simply by evaporating portions to dryness, and the labor thus involved is vastly less than that involved in the older method.<sup>1</sup>

While the Beckmann apparatus may be thus used with a large excess of ice, fairly accurate results may be obtained more simply as follows. A tall beaker of at least half a liter capacity is filled with finely cracked ice. In many cases a slight impurity present in the ice will not cause a serious error, unless the impurity present is such as to influence the degree of dissociation of the substance to be studied, or chemically to combine with it. It is important in this case, however, that the water at first surrounding the ice should have the same amount of impurity as the ice itself; hence, it is well to use a melted sample of the same material for this purpose. The beaker is surrounded by a protection of wool or cotton several centimeters thick, in order to delay the melting. The temperature of the melting ice is then taken by means of a deeply immersed accurate thermometer, allowing the zero point to become constant. A small portion of the substance to be studied, dissolved in a small volume of the same water, is added and the mixture is stirred with a pipette until the temperature has become approximately constant, and then the pipette is freed from the little cold liquid which it contains and quickly used to draw out its volume of liquid from the immediate neighborhood of the thermometer bulb. The thermometer, which of course should be gently tapped before each reading, remains surprisingly constant during this process, since the slow melting takes place only on the sides and top of the beaker, and the diffusion through the inter-

<sup>1</sup> Roloff thus analyzed concentrated solutions. *Ztschr. Phys. Chem.*, 18, 572 (1895). A. A. Noyes has kindly suggested to me the use of electrical conductivity as a convenient means of analyzing the solution without withdrawing it.

stices of the ice is too slow to have an important effect. If this withdrawn pipetteful measured 10 cc. and is titrated by means of an N/10 solution, the number of cubic centimeters of titrating solution divided by 100 gives at once the approximate equivalent normality of the freezing solution. For the greatest accuracy, of course, allowance should be made for the contraction of the glass and of the solution at the low temperature; but for approximate results these complications are not necessary. By means of this very simple apparatus it is easy to obtain a depression of half a degree within half a per cent. of its true value.

When it is desired to obtain a result accurate to within less than the thousandth of a degree, greater precautions of all kinds must be taken. The thermometer must become seasoned to the low temperature by remaining for hours, or even for days, in melting ice, in order that the slow rise of the zero point due to the slow internal adjustment of the glass may have ceased; the pressure due to the atmosphere and the height of the liquid should be carefully observed, since the bulb is compressible; the thermometer should be carefully calibrated with reference to the international hydrogen scale; the inflow and outflow of heat should be reduced to a minimum, and pure ice must be used. No thermometer can ever give an accurate reading of a temperature which is not constant for many minutes, because the thermometer possesses heat capacity, and its temperature must therefore inevitably lag behind that of its changing environment.<sup>1</sup>

The inflow or outflow of heat may easily be prevented by immersing the experimental vessel in a mixture possessing a temperature, within a few hundredths of a degree, the same as that inside. Such a mixture is very easily made with pounded ice and small portions of any soluble salt, added in solution until an auxiliary thermometer graduated into tenths of a degree indicates a sufficient approach to the temperature desired.<sup>2</sup> An air jacket, such as is used in Beckmann's apparatus, is an advantage, if it can be entirely immersed in this bath, but if it allows the convection of warm air it is rather a disadvantage than an advantage. A Dewar flask might answer well. For results of the greatest accuracy, the vessels should all be large. If these principles are heeded, almost any form of apparatus will yield good results.

<sup>1</sup> This error greatly complicates the correction for cooling in calorimetric experiments, but is usually disregarded.

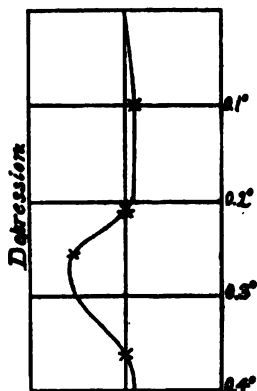
<sup>2</sup> Nernst and Abegg used constant temperature-baths of this kind (*loc. cit.*).

The determinations recorded below were conducted as follows: A Jena flask holding somewhat over a liter, was fitted with a rubber stopper containing three holes. One of these received the thermometer (which was arranged so as to come no nearer than a centimeter to the bottom of the flask), another a short fine funnel-tube for admitting the salt solution, and the third a short, wide glass tube large enough to admit the long stem of a 20 cc. pipette. This pipette was used for withdrawing portions of the solution, its point was always allowed to remain several minutes in the ice, and the liquid remaining in it was always expelled, before it was filled by suction. If the flask has not a wide neck, the stem of the pipette should be slightly bent just below the bulb, otherwise this bulb collides with the projecting thermometer stem.

During an experiment, the flask was somewhat more than half-filled with carefully washed, cracked ice, and at first contained enough ice-water to reach about a centimeter above the top of the thermometer bulb,—enough to render the pieces of ice easily mobile. The flask was then immersed in a large bath of similar cracked ice, and was packed in cotton wool and cloth and left with the thermometer stem projecting for forty-eight hours. In this time, the arbitrary zero point of the thermometer rose from a minimum of 3.805 to 3.820, where it remained during the experiments, so long as there was no large change in the pressure on the bulb. When the zero point had been established, successive portions of potassium chloride solution were added, and the corresponding positions of the mercury thermometer were read after suitable agitation and delay. The contents of the flask were easily mixed by removing it from the ice-bath and giving it a rotary motion. As already suggested, the ice-bath was provided with an essentially isotonic solution by stirring in dilute salt solution until an auxiliary thermometer indicated about the same depression in the outside bath as that exhibited by the accurate thermometer within the flask. Constancy was usually reached within five or six minutes from the introduction of the dissolved substance. The successive change in concentration might be most conveniently effected by adding successive portions of the solution, having the same volumes as that previously removed by the pipette. If the solution were cooled before its introduction, the amount of ice would remain nearly constant, although hardly constant enough to dispense with the analysis of the solution.

The thermometer used in these experiments was one of the Beckmann type, made by F. O. R. Götze in 1895, divided into hundredths of a degree. In order to make certain of the value of its degree, it was compared with thermometer Baudin 15275, which was made and standardized with the greatest precision by the Bureau International des Poids et Mesures for this purpose.<sup>1</sup> The following table and accompanying diagram gives the results of this comparison, which was made after both thermometers had been in ice for a long time. The bath in which they were compared consisted of properly protected and stirred ice fragments immersed in suitably dilute solutions of salt. The readings were made with an accurate Geneva microscope-micrometer.

Beckmann thermometer.	Standard thermometer (corrected).	Correction to be applied to Beckmann. -0.01° ← correction → +0.01°.
3.820°	+0.107°	
3.817°	+0.104°	
3.718°	+0.004°	
3.604°	-0.110°	
3.559°	-0.148°	
3.456°	-0.257°	
3.100°	-0.617°	



This table was verified by measuring lengths of short mercury columns in various places, a process which indicated a narrow place in the bore between 3.60° and 3.50°; but nevertheless this question of calibration is the most serious difficulty in the whole matter. Its import is so great as to make the present paper a preliminary one rather than a final statement of the depressions corresponding to definite solutions. According to the method described there is no difficulty in attaining a great degree of constancy in the thermometer readings; but to determine the true temperature from these readings is a far more difficult problem. The thermometer bulb was not allowed to become warm throughout the series of experiments, for fear of changing the settled structure of the cold glass. The correction for the projecting thread of the thermometer was eliminated by the constancy of the conditions.

Potassium chloride was chosen as the substance to be studied in order to facilitate comparison with the work of other experi-

<sup>1</sup> See *Proc. Am. Acad.*, 38, 434 (1902).

menters, who have nearly always used it as one of their substances. The specimen employed was precipitated by hydrochloric acid from a pure solution, and thoroughly dried. The amounts present in the respective solutions were determined by a modified form of Vohard's method, titrating the excess of standard silver nitrate with sulphocyanate, after filtering off the precipitated silver chloride, which otherwise disturbs the reaction by its solubility. The solutions were standardized in a similar way with pure fused potassium chloride. Since the solutions were  $N/5$ , and the instruments were accurate,<sup>1</sup> the reading for the silver nitrate divided by 100 gives at once the normality of the freezing solutions.

Below is given a table of data and results which are enough to indicate the satisfactory constancy of the readings. An hour elapsed between the first and third experiments, as well as between the eighth and tenth. The atmospheric and hydrostatic pressure on the thermometer bulb were essentially constant.

No. of experiment.	Concentration of solution (normal standard).	Observed depression.	Corrected depression.	Molar depression.
1	0.1256	0.433°	0.433°	3.42
2	0.1261	0.433°		
3	0.1258	0.432°		
	0.1258	0.433°		
4	0.0944	0.330°	0.328°	3.48
5	0.0944	0.330°		
	0.0944	0.330°		
6	0.0386	0.136°	0.137°	3.52
7	0.0388	0.136°		
	0.0387	0.136°		
8	0.0311	0.112°	0.112°	3.59
9	0.0309	0.111°		
10	0.0307	0.111°		
	0.0309	0.111°		

These results are near those of other experimenters,\* who needed much more labor than that expended in the present case. For example, Abegg found, for the concentrations 0.0469 and 0.0354, molecular depressions of 3.47 and 3.50 respectively, results but slightly lower than those given above.

<sup>1</sup> The most important burette, that used for the silver nitrate, was unusually fine in bore and in graduation, having been marked only after careful preliminary calibration by the author.



While the study of a single electrolyte furnishes too meager a basis for extended theoretical conclusions, especially when the possible inaccuracy of the thermometer introduces a wide range of possible error, it may not be out of place to compare these molar depressions with those calculated from the conductivity. In order to make this comparison, it would be necessary to know the average molar depression caused by a non-electrolyte with an equal degree of accuracy. For the present the value,  $186^{\circ}$  taken from the average of many previous investigations, is sufficiently accurate. On this basis the degrees of dissociation of the four solutions whose depressions are recorded above are easily calculated as 0.84, 0.87, 0.89, and 0.93 respectively.

The most accurate data concerning the electrolytic conductivity of aqueous solutions are perhaps those of Kohlrausch and Maltby,<sup>1</sup> but unfortunately these do not apply in the present case, since the temperature used was  $18^{\circ}$ , not  $0^{\circ}$ . Next to these comes the work of Whetham,<sup>2</sup> who worked with very great care at the required temperature. He found the equivalent conductivity of potassium chloride to be 75.2 when diluted to 33 liters per mol, and to attain a maximum of 80.7 when diluted to 2000 liters. This leads to the value 0.93 for the degree of dissociation of the former solution, a solution which corresponds exactly to the last one named in the preceding paragraph.

The agreement between these two results (0.93 according to both the depression of the freezing-point and the electrical conductivity) is closer than would be expected from the possible errors of the results compared. So far as it goes, therefore, it is satisfactory to the adherent of the modern theory of solution; but many more comparable results with other substances should be obtained before the subject is allowed to drop.

The constancy of the thermometric readings obtained in this way from mixtures of ice with dilute solutions suggests the availability of such mixtures as a means of calibrating thermometers below the freezing-point. If an accurate curve were plotted, comparing the normality of the solution with the actual depression of the freezing-point, all that would be necessary in order to determine the error of a given point in a thermometer would be to place

<sup>1</sup> *Wiss. Abh. phys. tech. Reichsanstalt*, 3, 157 (1900).

<sup>2</sup> *Ztschr. phys. Chem.*, 33, 344 (1900). The work of Déguisne at  $2^{\circ}$  indicates essentially the same value as that of Whetham. (Inaug. Diss., Strassburg, 1895.) Unfortunately Déguisne has not presented his data, but has concealed them in quadratic equations.

it in pure ice and then to stir into the ice an increasing amount of the standard solute until the desired point on the thermometer was reached and maintained. An analysis of the commingled solution, with the help of the curve, would then at once give the temperature which the thermometer ought to have recorded, and hence the error of the given point on the thermometer. Hydrochloric acid would perhaps be the best substance for this purpose, since it is easily prepared in a pure state and may be determined volumetrically in a variety of ways.

Such a means of calibrating thermometers would be theoretically as exact as any other, for according to the phase rule, with two components, four conditions must be fixed in order to fix a point. In the present case, the four conditions would be two phases, pressure, and the concentration of the dissolved substance. The experience gained in the trials recorded above seems to indicate that this method is practically feasible as well as theoretically sound, and in the near future more accurate data concerning the true course of some such curve will be obtained here.

Besides this, it is my object to study with the help of the new method a number of electrolytes and non-electrolytes with all possible accuracy, using a platinum resistance thermometer.

#### SUMMARY.

It is pointed out that in the presence of much ice the equilibrium concerned in the freezing-point of solutions is obtained with great speed and convenience. Several forms of apparatus are suggested for this determination, and results are given, showing that the plan is capable of practical execution. The exactness seems to be so great that the method may be of use in standardizing thermometers. The few data found are consistent with the hypothesis of ionization.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 68.]

### DERIVATIVES OF NEW COMPLEX INORGANIC ACIDS.<sup>1</sup>

BY ALLEN ROGERS.

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THE splendid research work upon complex inorganic acids, by Dr. Wolcott Gibbs, has brought to view numerous classes of most

<sup>1</sup> From the author's thesis for the Ph.D. degree presented in June, 1902.

interesting bodies. So full of interest have they been that other students have ventured to enter the field and, as might be expected, have extended the limits of our knowledge in this particular domain of chemical science. Yet, the end seems not reached, for a glance at the ammonium vanadico-phospho-tungstate described by Smith and Exner<sup>1</sup> discloses again a new class or series of complex inorganic acids, in which there exists a triple complex acid. Wolcott Gibbs described somewhat similar bodies in which, however, the vanadium oxide present was the dioxide and not the trioxide as is the case with the compound isolated by Smith and Exner. To reproduce the body obtained by these chemists and gain further insight into its constitution and deportment was the primary purpose of the present investigation which has resulted in the discovery of a number of analogous derivatives, a description of which will now be given.

AMMONIUM PHOSPHO-VANADIO-TUNGSTATE,



*Preparation.*—In the preparation of this salt various amounts of ammonium phosphate, ammonium vanadate, and ammonium tungstate were boiled together for six hours. The solution, after filtration, was evaporated and allowed to crystallize. The crystals formed in every case were identical in physical appearance and, as will be seen later, had the same chemical composition.

The best results were obtained when 1 gram of ammonium phosphate, 15 grams of ammonium tungstate, 3 grams of ammonium vanadate, 20 cc. of ammonium hydroxide, and 700 cc. of water were brought together, in a liter flask, and boiled for six hours. At first the solution was colorless, but soon changed to yellow and then to red. At this point the ammonium tungstate dissolved very rapidly, and the solution became much darker in color. The slight residue was filtered off, and the filtrate evaporated to a specific gravity of 1.115. On standing over night, the salt separated. The mother-liquor was again evaporated, and a second crop of crystals was obtained.

*Properties.*—The product of the above procedure gave dark red-colored crystals, which were octahedra and cubes in form; very soluble in cold and hot water; insoluble in alcohol, ether, carbon disulphide, benzene, and nitrobenzene. No change was produced

<sup>1</sup> This Journal, 24, 573.

when the crystals, reduced to a fine powder, were treated with dilute nitric or hydrochloric acid. Strong hydrochloric acid gave a yellow precipitate, with the evolution of chlorine, on boiling. Strong nitric acid produced a yellow precipitate, which dissolved on the addition of water. With ammonium hydroxide, there was no change. Caustic potash or soda gave a yellow precipitate, which dissolved on boiling, with the evolution of ammonia. Mercurous nitrate formed a yellow precipitate, which turned red when dry; insoluble in boiling water or an excess of the reagent; but rendered soluble by a few drops of nitric acid. This precipitate was found to be the mercury salt of phospho-vanadio-tungstic acid, and from it the acid was prepared. A discussion of this acid, and its salts with the heavy metals, is not within the scope of this paper. It may not, however, be out of place to give some of the principal points at this time. Starting with ammonium phospho-vanadio-tungstate, the silver or mercury (better silver) salt was precipitated. This precipitate was washed, and dried; or, in most cases, was placed in a flask with a few drops of nitric acid and brought to boiling. When the solution was complete, it was filtered and evaporated to a small volume, and, on standing over night, crystals of silver phospho-vanadio-tungstate were deposited. These crystals were removed and dissolved in water, and to the solution hydrochloric acid was added, a few drops at a time, until all of the silver was precipitated. The silver chloride was filtered off and the filtrate evaporated on the water-bath to a small volume. From this solution the acid was deposited in dark red, octahedral crystals. A solution of this acid gave the same reaction with the heavy metals as those produced by the ammonium salt. With ammonium phospho-vanadio-tungstate, and also with phospho-vanadio-tungstic acid the precipitates formed were found to be due to the deposition of metallic derivatives of the above-mentioned acid.

To come back to the ammonium salt again: It was found that copper nitrate produced no change in the solution; but when ammoniacal copper nitrate was added, a red precipitate was formed, insoluble in boiling water, but dissolving very readily when a few drops of nitric acid were added. Ammoniacal cadmium chloride gave an orange-colored precipitate, slightly soluble in boiling water; but very soluble in nitric acid. Stannous chloride gave a gray precipitate, rapidly taking on a blue tint. Am-

moniacal cobalt nitrate produced a greenish gray precipitate, which turned red when dried. Zinc acetate gave a yellow precipitate quite soluble in boiling water. Barium chloride, in an ammoniacal solution, gave a light yellow precipitate, which remained insoluble on boiling, but dissolved readily when a little nitric acid was added.

*Method of Analysis.*—The methods proposed by Gibbs<sup>1</sup> and Friedheim<sup>2</sup> could not be used in the analysis of the black crystals obtained by Smith and Exner; neither were they applicable to this salt. After trying various means the following was found to give very satisfactory results:

The air-dried salt was reduced to a fine powder, and a known quantity introduced into a tared crucible. It was heated gently at first, then the temperature was increased, and continued until constant weight was obtained. The loss represented the water and ammonium oxide. The residue was boiled with dilute nitric acid in which the vanadium pentoxide and phosphorus pentoxide dissolved, leaving the tungsten trioxide insoluble. After standing several hours, the precipitate was filtered off. It was washed with a little water containing nitric acid, dried, ignited, and weighed as tungsten trioxide. The tungsten trioxide nearly always held some vanadium pentoxide which was removed by gently heating in a current of hydrochloric acid gas. The filtrate from the tungsten trioxide was evaporated to dryness in a weighed porcelain crucible on the water-bath, and then gently heated over the flame. The mass fused. In this way the combined weight of the phosphorus pentoxide and vanadium pentoxide was determined. The fusion was taken up with water containing a little nitric acid, in which it dissolved readily on warming. The phosphorus pentoxide was thrown out with a magnesia mixture. The ammonium magnesium phosphate was dissolved in dilute nitric acid, and reprecipitated by addition of ammonium hydroxide, when it came down free from vanadium. The vanadium pentoxide was then determined by difference. To make sure, however, that the difference was vanadium pentoxide, in a number of cases, vanadium was thrown out from the filtrate, with concentrated ammonium chloride and alcohol. On ignition of the ammonium vanadate so found vanadium pentoxide was produced, which in

<sup>1</sup> *Am. Chem. J.*, 1, 217; 2, 217, 281; 3, 119; 4, 377; 5, 391; 7, 313, 392.

<sup>2</sup> *Ber. d. chem. Ges.*, (1890), pp. 352, 1503, 1530, 2600.

each case corresponded to the amount obtained by difference. The ammonium oxide was ascertained by boiling a new portion of the salt with caustic potash, the liberated ammonia being collected in a standard solution of hydrochloric acid, and the excess titrated with ammonium hydroxide. The ammonium oxide found by this means was subtracted from the ammonium oxide and the water determined by ignition. The difference gave the true water content.

*Result of Analysis.*—The percentages as given below are for salts prepared from eight different combinations. It shows, therefore, that the same compound was always produced.

	Theory.	Found.							
$(\text{NH}_4)_2\text{O} \dots$	5.71	5.72	5.77	5.77	5.57	5.87	5.59	5.59	5.89
$\text{P}_2\text{O}_5 \dots \dots$	2.39	2.32	2.60	2.60	2.43	2.52	2.33	2.51	2.25
$\text{V}_2\text{O}_5 \dots \dots$	12.28	12.09	12.25	11.91	12.50	12.23	12.03	11.68	12.07
$\text{WO}_3 \dots \dots$	66.55	66.33	66.39	66.32	66.35	66.44	66.41	66.39	66.35
$\text{H}_2\text{O} \dots \dots$	13.07	13.17	12.78	13.16	13.09	12.97	13.63	13.77	12.84
	100.00	99.63	99.89	99.76	99.94	100.03	99.99	99.94	99.40

SILVER PHOSPHO-VANADIO-TUNGSTATE,



When silver nitrate is added to a solution of ammonium phospho-vanadio-tungstate a brick-red precipitate is formed, which is soluble to some extent in water, and is completely dissolved by water to which a few drops of nitric acid are added. The compound is obtained pure by washing with water until the wash-water gives no test for nitric acid. The following method of analysis may be employed:

*Method of Analysis.*—Have the precipitate dried at  $70^\circ$  for one hour after being air-dried, in the state of a fine powder, and heat a weighed amount of it to dull redness; the loss will give the amount of water of crystallization. Another portion is dissolved in water containing a few drops of nitric acid; then hydrochloric acid is added to remove the silver as silver chloride. The filtrate from the silver chloride is evaporated to dryness in a weighed crucible with a little nitric acid, and the weight, after strongly heating, represents the combined tungsten trioxide, phosphorus pentoxide and vanadium pentoxide. This mass is then digested with dilute nitric acid, and the tungsten trioxide filtered off and weighed; as this trioxide may contain a little

vanadium pentoxide, it is always necessary to heat in a current of hydrochloric acid to remove the last trace of vanadium. The filtrate from the tungsten trioxide is treated with ammonium hydroxide to alkaline reaction, and the magnesia mixture added to throw out the phosphoric acid. As the magnesium ammonium phosphate also contains some vanadium, it is necessary to dissolve it and reprecipitate. The amount of vanadium pentoxide is determined by difference, *i. e.*, the phosphorus pentoxide plus the tungsten trioxide, subtracted from the total phosphorus pentoxide, vanadium pentoxide, and tungsten trioxide.

## RESULTS OF ANALYSIS.

	Theory.	Found.							
Ag <sub>2</sub> O .....	22.93	22.81	22.66	21.91	22.44	23.17	22.83	23.17	
P <sub>2</sub> O <sub>5</sub> .....	2.15	2.18	2.14	2.12	2.19	2.01	2.21	2.08	
V <sub>2</sub> O <sub>5</sub> .....	11.09	11.23	11.09	13.31	12.17	11.17	11.21	11.25	
WO <sub>3</sub> .....	58.22	58.01	58.11	57.56	57.66	58.02	58.17	58.05	
H <sub>2</sub> O .....	5.61	5.59	5.51	5.73	5.65	5.53	5.57	5.47	
	100.00	99.82	99.51	100.63	100.11	99.90	99.99	99.97	

In this case, a mean of the results is taken for the derivation of the formula and corresponds very closely with that found for the ammonium salt. The difference of 1 molecule of tungsten trioxide may be eliminated if a number of the results under the analysis of the ammonium salt had been chosen for the calculation instead of a mean of all them.

It will be observed that red-colored salts were obtained by the methods pursued in the preceding paragraphs, while the ammonium salt described by Smith and Exner had a deep black color. Later, it was discovered that this color was caused by the reduction of the vanadium to a lower oxide; therefore, the following salt was prepared:

## AMMONIUM PHOSPHO-VANADICO-TUNGSTATE,



*Preparation.*—The salt was obtained by bringing together 1 gram of ammonium phosphate, 15 grams of ammonium tungstate, 1.1 grams of vanadium trioxide (prepared by heating 1.6 grams of ammonium vanadate with strong hydrochloric acid, and evaporating to dryness on a water-bath), 25 cc. of ammonium hydroxide with 700 cc. of water, and boiling the mixture for six hours. By

this means a black-colored solution resulted, which was evaporated to a specific gravity of 1.030 and allowed to stand over night in a cool place. The crystals obtained had a deposit of ammonium chloride on the surface. This was removed by washing them with a little cold water, and the product was finally dried on filter-paper.

*Properties.*—The salt as prepared in the above manner gave black crystals with octahedral and cubic habit, the octahedral being far in excess and truncated by the faces of the cubes. The compound was soluble in water; insoluble in alcohol, ether or benzene. Dilute nitric acid produced a slight change in color on boiling. The same thing occurred with dilute hydrochloric acid. Strong hydrochloric acid produced a yellow precipitate, but without the evolution of chlorine on boiling. Concentrated nitric acid gave a yellow precipitate, which dissolved on adding water. Ammonium hydroxide produced no change. Potassium hydroxide gave a yellow precipitate, which partly dissolved on boiling, at the same time giving off ammonia, while a black residue remained. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved on adding a little nitric acid. Silver nitrate gave a greenish black precipitate. Barium chloride produced a gray precipitate which dissolved when heated, but separated again on cooling. The composition of the salt was very much like that obtained from the mother-liquor of ammonium paratungstate by Smith and Exner, but differed from it in some of its properties.

*Method of Analysis.*—The same method was applied as for the first salt, except that the resulting vanadium pentoxide was calculated into vanadium trioxide, and the difference added to the percentage of water of crystallization.

	Theory.	Found.				
$(\text{NH}_4)_2\text{O}$ .....	5.53	5.44	5.44	5.32	5.32	5.35
$\text{P}_2\text{O}_5$ .....	2.02	1.94	2.03	1.84	1.94	1.94
$\text{V}_2\text{O}_5$ .....	6.39	6.34	6.34	6.32	6.06	6.26
$\text{WO}_3$ .....	72.50	72.34	72.23	72.55	72.99	72.52
$\text{H}_2\text{O}$ .....	13.56	13.60	13.59	13.43	13.69	13.55
	100.00	99.66	99.63	99.46	100.00	99.62

#### AMMONIUM PHOSPHORICO-VANADIO-TUNGSTATE.

It was thought that this salt would result when ammonium



phosphite, ammonium tungstate and ammonium vanadate were brought together. Such, however, was not the case. The compound produced proved to be ammonium phospho-vanadico-tungstate. This, no doubt, was due to the reducing action of phosphorus trioxide on vanadium pentoxide.

AMMONIUM PHOSPHORICO-VANADICO-TUNGSTATE,



*Preparation.*—The next thought to present itself for consideration was to see if a salt could be prepared having the phosphorus and vanadium both in the lower state of oxidation. To accomplish this, 1.5 grams of ammonium phosphite, 1 gram of vanadium trioxide, 20 grams of ammonium tungstate, 25 cc. of ammonium hydroxide, and 700 cc. of water were brought together. After boiling for five hours, the black-colored solution was filtered, and evaporated to about one-fourth of its original volume.

*Properties.*—The resulting black octahedral crystals were soluble in water; insoluble in alcohol, ether, carbon disulphide, and benzene. The action of dilute or strong nitric or hydrochloric acid, mercurous nitrate, or even silver nitrate was the same as in the previous salt. Barium chloride produced no change when first added to the solution; on standing, an olive-green precipitate was formed.

*Method of Analysis.*—The same method was used as in former cases; except that a few drops of nitric acid were added to the mass after ignition. The excess of acid was driven off by warming in the water-bath, and the crucible again strongly heated. The resulting vanadium pentoxide and phosphorus pentoxide were calculated to vanadium trioxide and phosphorus trioxide, the difference being added to the percentage of water.

These seem to be all of the possible combinations in this series; that is, in which we have one base united to one oxide of each of the three acid-forming elements.

RESULT OF ANALYSIS.

	Theory.	Found.				
$(\text{NH}_4)_2\text{O}$ .....	6.85	6.80	6.86	6.86	6.75	6.75
$\text{P}_2\text{O}_5$ .....	2.07	2.03	2.02	1.94	2.11	2.00
$\text{V}_2\text{O}_5$ .....	9.89	10.08	10.21	10.06	9.91	9.38
$\text{WO}_3$ .....	67.98	67.91	67.73	66.77	68.11	68.02
$\text{H}_2\text{O}$ .....	13.21	12.93	12.45	12.77	12.74	13.74
	100.00	99.75	99.54	99.40	99.62	99.89

It has been demonstrated that phosphorus, vanadium, and tungsten combine to form a series of complex inorganic acids. These acids have also been shown to be stable bodies, and capable of giving salts with many basic radicals. The reactions obtained with the heavy metals show a difference from those produced by salts of any of the individual members. The conclusion drawn from these reactions and the constant composition given by analysis is that the compounds under consideration are definite bodies, and not mixtures of phosphates, vanadates, and tungstates.

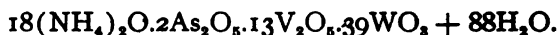
In the same group with phosphorus is arsenic. This element has many properties in common with phosphorus. The question arose: Can we have a series of compounds in which arsenic takes the place of the phosphorus? The idea appeared to be plausible. Ammonium arsenate and ammonium arsenite were, therefore, substituted for the corresponding phosphorus salt and the following series of compounds prepared:

*Ammonium arseno-vanadio-tungstate.*

*Ammonium arseno-vanadico-tungstate, and*

*Ammonium arsenico-vanadico-tungstate.*

#### AMMONIUM ARSENO-VANADIO-TUNGSTATE,



*Preparation.*—To 700 cc. of water, made alkaline with 15 cc. of ammonium hydroxide, 1 gram of ammonium arsenate, 15 grams of ammonium tungstate and 1 gram of ammonium vanadate were added. The mixture was heated to boiling and maintained at that temperature for five hours. The solution was, at first, colorless, but soon changed to yellow, and then to red, but the red was not as intense as in the case of the phospho-salt. The filtered solution was evaporated and on standing over-night the salt separated.

*Properties.*—The small octahedral crystals which were formed above were soluble in water, but insoluble in organic solvents. Dilute hydrochloric acid or nitric acid was without action. When boiled with strong hydrochloric acid, chlorine was evolved, and a yellow precipitate produced; on further boiling, the precipitate dissolved, but reappeared when the solution had become cold, or on the addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. From this precipitate it seems probable

that the acid can be obtained. Silver nitrate gave a red precipitate, soluble in boiling water, hastened by a drop or two of nitric acid. Lead acetate, ammoniacal copper nitrate or other salts of the heavy metals gave precipitates, which resembled those obtained from the corresponding phospho-compound. As far as studied, these precipitates were derivatives of arseno-vanadio-tungstic acid. A more complete study, however, may bring out many interesting facts. But as the purpose of this paper is to point to the different possibilities, rather than to go too much into detail, we will leave the thought, and, as time goes on, and more work is carried out in this line of investigation, let us hope that the gaps may be filled, and that the completed structure may have its proper place in the great family of inorganic compounds.

*Method of Analysis.*—The same procedure was employed as for the phospho-salts.

## RESULT OF ANALYSIS.

	Theory.	Found.				
$(\text{NH}_4)_2\text{O}$ .....	6.51	6.63	6.63	6.73	6.73	6.68
$\text{As}_2\text{O}_5$ .....	3.18	3.17	2.94	3.11	3.11	3.08
$\text{V}_2\text{O}_5$ .....	16.39	16.80	16.75	16.22	16.26	16.51
$\text{WO}_3$ .....	62.95	62.70	62.75	62.81	62.86	62.80
$\text{H}_2\text{O}$ .....	10.97	10.54	10.51	10.83	10.58	10.61
	100.00	99.84	99.58	99.70	99.54	99.68

## AMMONIUM ARSENO-VANADICO-TUNGSTATE,



*Preparation.*—In the synthesis of this body 1 gram of ammonium arsenate, 15 grams of ammonium tungstate, 1 gram of vanadium trioxide, 25 cc. of ammonium hydroxide and 700 cc. of water were boiled for five hours. The filtered solution was evaporated on the water-bath to about one-half of the original volume. It was then removed to a cool place and allowed to stand over night. The crystals were usually covered with a deposit of ammonium chloride which was removed by a little cold water. The crystals from the mother-liquor were often mixed with other salts. In order, therefore, to get concordant results, crystals of the first crop were submitted to analysis.

*Properties.*—The salt, as prepared above, consisted of black octahedral forms, sparingly soluble in cold water; readily soluble in boiling water; insoluble in alcohol, ether, benzene, carbon di-

sulphide, chloroform, acetone, acetic anhydride, nitrobenzene, and aniline. Dilute nitric acid produced a change in color from black to red. Dilute hydrochloric acid changed the color likewise when it was boiled with this reagent. Strong nitric acid gave a yellow precipitate, which dissolved on the addition of water. Strong hydrochloric acid gave a yellow precipitate. Mercurous nitrate produced a red precipitate, which remained insoluble on boiling, but dissolved when nitric acid was added. Silver nitrate gave a dark green precipitate. An attempt was made to get the acid from this salt, but through the action of nitric acid an oxidation took place, the result being that arseno-vanadio-tungstic acid was produced. It may be possible, however, to liberate arseno-vanadico-tungstic acid by some other method, and from the acid so obtained many new compounds would result.

*Method of Analysis.*—The method used for the corresponding phospho-salt was employed in this case.

#### RESULT OF ANALYSIS.

Theory.	Found.				
$(\text{NH}_4)_2\text{O} \dots\dots$	7.34	7.26	7.25	7.29	7.29
$\text{As}_2\text{O}_5 \dots\dots\dots$	3.82	3.77	3.80	3.77	3.62
$\text{V}_2\text{O}_5 \dots\dots\dots$	18.06	18.11	18.06	17.33	18.17
$\text{WO}_3 \dots\dots\dots$	56.12	56.04	55.99	56.04	56.07
$\text{H}_2\text{O} \dots\dots\dots$	14.66	14.41	14.46	14.35	14.40
	100.00	99.59	99.56	99.78	99.55

#### AMMONIUM ARSENICO-VANADIO-TUNGSTATE.

By analogy, the production of this compound was looked upon as improbable. A mixture, however, of ammonium arsenite, ammonium vanadate and ammonium tungstate was boiled for six hours. The solution turned dark in color, and finally became black, due to the formation of ammonium arseno-vanadico-tungstate. It may be possible, however, under proper conditions to obtain this salt, as the reduction is not so marked as in the case of the ammonium phosphorico-vanadio-tungstate.

#### AMMONIUM ARSENICO-VANADICO-TUNGSTATE,



*Preparation.*—In the production of this compound the same line of thought suggested itself as in case of the corresponding phosphorico-salt. If vanadium could unite with arsenic as arsenic

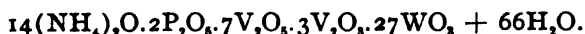
pentoxide in two ways, it seemed probable that it would unite with it as arsenic trioxide. A number of different combinations were tried to determine this, but on boiling together 1 gram of arsenic trioxide, 12 grams of ammonium tungstate, 1 gram of vanadium trioxide, 50 cc. of ammonia and 700 cc. of water, the best results were obtained. After boiling for five hours, the solution was evaporated to about one-half its original volume. On standing in a cool place for twenty-four hours the salt separated.

*Properties.*—Black octahedral crystals sparingly soluble in cold water, which dissolved readily when boiled. Dilute nitric acid produced a change in color. Strong hydrochloric acid gave a yellow precipitate. Nitric acid gave a yellow precipitate, which remained insoluble on boiling, but dissolved when water was added. Silver nitrate produced a greenish black precipitate, which readily dissolved on the addition of a little nitric acid. Barium chloride gave a gray precipitate, insoluble on boiling; readily soluble in dilute nitric acid.

## RESULT OF ANALYSIS.

	Theory.	Found.		
$(\text{NH}_4)_2\text{O}$ .....	6.96	7.02	7.02	7.02
$\text{As}_2\text{O}_3$ .....	8.28	8.26	8.12	8.41
$\text{V}_2\text{O}_5$ .....	18.83	18.97	18.95	18.99
$\text{WO}_3$ .....	50.70	50.69	50.57	50.71
$\text{H}_2\text{O}$ .....	15.23	15.18	15.23	15.13
	100.00	100.12	99.89	100.26

## AMMONIUM PHOSPHO-VANADIO-VANADICO-TUNGSTATE,



*Preparation.*—After proving that compounds could exist in which the phosphorus and vanadium were in either state of oxidation, the question arose: Can a compound be prepared in which the same element is present in both conditions? It seemed possible, as Gibbs has shown, that such bodies can exist. It remained to determine if the presence of phosphorus would have any effect on the combination. For the preparation of this salt, 1 gram of ammonium phosphate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide, and 700 cc. of water were used. This mixture was boiled for five hours. The solution was then filtered, and the greenish black liquid was evaporated on the water-bath;

when reduced to about one-half of the original volume it was set aside to crystallize.

*Properties.*—The product obtained from the above solution gave greenish black octahedral crystals, which were sparingly soluble in cold water, but dissolved on boiling. Dilute nitric acid or hydrochloric acid changed the color to red. Strong hydrochloric acid decomposed it, with the evolution of chlorine. Strong nitric acid gave off fumes of nitrogen peroxide, while a green precipitate was produced, which dissolved on addition of water. Mercurous nitrate gave a yellow precipitate, which remained insoluble on boiling; but dissolved when nitric acid was added. Barium chloride produced a greenish gray precipitate, which dissolved on boiling, but reappeared when cooled.

*Method of Analysis.*—The procedure was, for the most part, the same as in former cases. The total vanadium was determined as vanadium pentoxide. A separate portion was boiled with hydrochloric acid, when vanadium pentoxide was reduced to vanadium dioxide, with the elimination of chlorine. The evolved gas was conducted into a solution of potassium iodide, and the liberated iodine titrated with standard sodium thiosulphate.

$$I_2 : V_2O_5 :: \text{Amt. of } Na_2S_2O_3 \times \text{Strength} : x.$$

The true amount of vanadium pentoxide was thus ascertained. This result subtracted from the total vanadium gave the vanadium pentoxide from which the vanadium trioxide was calculated.

#### RESULT OF ANALYSIS.

	Theory.	Found.		
$(NH_4)_2O$ .....	7.14	7.34	7.23	7.23
$P_2O_5$ .....	2.78	2.66	2.74	2.57
$V_2O_5$ .....	12.50	12.62	12.68	12.68
$V_2O_3$ .....	4.41	4.33	4.36	4.17
$WO_3$ .....	61.48	61.28	61.40	61.15
$H_2O$ .....	11.69	11.64	11.55	11.80
	100.00	99.87	99.96	99.60

#### AMMONIUM ARSENO-VANADO-VANADICO-TUNGSTATE,



*Preparation.*—From the readiness with which arsenic entered into combination in the salts already studied, it seemed likely that a body related to the one just described could be prepared by introducing arsenic pentoxide in place of phosphorus pentoxide.

This was accomplished by using 1 gram of ammonium arsenate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide, and 700 cc. of water.

The boiling was continued for four hours. The solution, which was greenish black in color, was evaporated on the water-bath until it had reached about one-half its original volume. It was then filtered while hot; and being placed in a crystallization dish, was set aside to cool. In most cases, at the end of twenty-four hours the salt had separated. The mother-liquor was again evaporated and a second crop of crystals was obtained. The yield of salt was much larger in these vanadio-vanadico-compounds than in the vanadico salt.

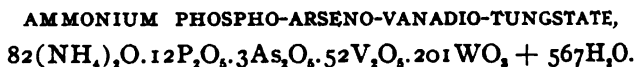
*Properties.*—The body produced in this case gave crystals which were black in color, and belonged to the same class as in former cases. The deposit of ammonium chloride was removed by washing with cold water. The solubility was the same as usual. Dilute nitric or hydrochloric acid changed the color of the solution from black to light red. Strong hydrochloric acid decomposed the salt, giving off chlorine, and producing a bright yellow precipitate of the hydrated oxide. Nitric acid gave an orange-colored precipitate, soluble on the addition of water. Mercurous nitrate, and barium chloride gave olive-green colored precipitates insoluble in boiling water, but soluble on the addition of a few drops of nitric acid.

## RESULT OF ANALYSIS.

	Theory.	Found.		
$(\text{NH}_4)_2\text{O}$ .....	7.41	7.42	7.42	7.42
$\text{As}_2\text{O}_5$ .....	3.84	3.71	3.79	3.63
$\text{V}_2\text{O}_5$ .....	10.65	10.36	10.26	10.26
$\text{V}_2\text{O}_3$ .....	5.02	5.26	5.32	5.27
$\text{WO}_3$ .....	62.09	62.12	62.04	62.20
$\text{H}_2\text{O}$ .....	10.99	10.94	10.95	10.15
	100.00	99.81	99.78	99.73

It was impossible to introduce phosphorus or arsenic in two conditions, at the same time having vanadium present as vanadium pentoxide, the reason for this being that a reduction of the vanadium pentoxide took place. At the same time the phosphorus or arsenic was oxidized to the higher condition. Were it not for the strong reducing action of arsenic trioxide and phosphorus

trioxide we could expect to obtain six new salts in the above manner. As a matter of fact, it was only possible to get two.



*Preparation.*—After having obtained salts, in which the vanadium was present in two states of oxidation, the question arose: Is it possible to have phosphorus and arsenic together with the vanadium? It remained to ascertain if the arsenic and phosphorus would unite, or if the phosphorus would produce one body, and the arsenic another. This could only be determined by analysis of the first and second crop of crystals.

In the preparation of the salt, 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 2 grams of ammonium vanadate, 16 grams of ammonium tungstate, 20 cc. of ammonium hydroxide, and 700 cc. of water were boiled for six hours. The solution, which had taken on a deep red color, was filtered while hot. It was then evaporated to one-fourth of its original volume, and on standing over night, the salt was deposited. A second crop of crystals was obtained from the mother-liquor. These were placed in a separate bottle, for the reason given above.

*Properties.*—The salt so prepared consisted of dark red crystals which were octahedral in form, very soluble in warm water, but insoluble in organic solvents. Dilute nitric or hydrochloric acid was without action. Strong hydrochloric acid produced a yellow precipitate with the evolution of chlorine. Strong nitric acid gave a precipitate, soluble on the addition of water. Mercurous nitrate gave an orange-colored precipitate, insoluble on boiling, but rendered soluble by the addition of a few drops of nitric acid. Barium chloride produced no change in the cold, but on warming, a light yellow precipitate came down.

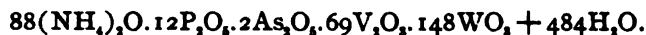
*Method of Analysis.*—The salt was treated as in former cases, except that the magnesium pyrophosphate and magnesium pyroarsenate, after weighing, were dissolved in hydrochloric acid and hydrogen sulphide passed through the solution to throw out the arsenic. Thus phosphorus pentoxide was determined by throwing out the magnesium pyrophosphate again, giving the arsenic and phosphorus either direct or by difference.



## RESULT OF ANALYSIS.

	Theory.	Found.			
$(\text{NH}_4)_2\text{O}$ .....	5.82	5.81	5.79	5.79	5.84
$\text{P}_2\text{O}_5$ .....	2.32	2.24	2.26	2.22	....
$\text{As}_2\text{O}_5$ .....	0.98	0.98	1.00	0.81	....
$\text{V}_2\text{O}_5$ .....	12.95	13.07	13.05	13.09	....
$\text{WO}_3$ .....	63.98	63.85	63.86	63.67	63.91
$\text{H}_2\text{O}$ .....	13.95	13.87	13.88	13.85	....
	100.00	99.82	99.84	99.35	

## AMMONIUM PHOSPHO-ARSENO-VANADICO-TUNGSTATE,



*Preparation.*—Having made the combination of phosphorus pentoxide, arsenic pentoxide, and vanadium pentoxide, the next step was to introduce the vanadium as the trioxide. For this purpose 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 2 grams of vanadium trioxide, 16 grams of ammonium tungstate, 30 cc. of ammonium hydroxide and 700 cc. of water were boiled for four hours. The greenish black solution was filtered while hot. It was then evaporated to about one-half of its original volume, and on standing over night, in a cool place, the salt separated. The second crop of crystals was contaminated with impurities, and could not be used for analysis.

*Properties.*—Greenish black, octahedral crystals, soluble in water, insoluble in alcohol or ether. Dilute nitric or hydrochloric acid was without action. Strong hydrochloric acid gave a red solution, with only a slight cloudiness being formed; on addition of water a heavy yellow precipitate came down. The precipitate produced by nitric acid dissolved on the addition of water. Mercurous nitrate and barium chloride produced yellow precipitates, which remained insoluble on boiling, but dissolved when a little nitric acid was added.

## RESULT OF ANALYSIS.

	Theory.	Found.		
$(\text{NH}_4)_2\text{O}$ .....	7.59	7.58	7.52	7.58
$\text{P}_2\text{O}_5$ .....	2.82	2.88	2.81	2.84
$\text{As}_2\text{O}_5$ .....	0.76	0.76	0.73	0.66
$\text{V}_2\text{O}_5$ .....	17.16	17.09	17.11	17.17
$\text{WO}_3$ .....	57.20	57.11	57.15	56.89
$\text{H}_2\text{O}$ .....	14.47	14.38	14.36	14.24
	100.00	99.80	99.68	99.38

AMMONIUM PHOSPHO-ARSENO-VANADIO-VANADICO-TUNGSTATE,  
 $99(\text{NH}_4)_2\text{O} \cdot 12\text{P}_2\text{O}_5 \cdot 2\text{As}_2\text{O}_5 \cdot 66\text{V}_2\text{O}_5 \cdot 6\text{V}_2\text{O}_6 \cdot 191\text{WO}_3 + 522\text{H}_2\text{O}$ .

*Preparation.*—From the previous salts produced, it seemed possible to introduce vanadium in two conditions together with the phosphorus and arsenic.

To accomplish this 1 gram of ammonium phosphate, 1 gram of ammonium arsenate, 1 gram of ammonium vanadate, 1 gram of vanadium trioxide, 16 grams of ammonium tungstate, 20 cc. of ammonium hydroxide, and 700 cc. of water were boiled together for six hours. The filtered solution was evaporated, and allowed to stand over night to crystallize.

*Properties.*—The yield of salt was small. Black octahedral crystals, however, separated. On evaporation of the mother-liquor the crystals, which were minute, were mixed with a large amount of other salts, from which it was difficult to separate them.

The deposit of ammonium chloride, as well as other impurities, were removed to some extent by washing with cold water, in which the crystals themselves were not very soluble. Strong hydrochloric acid decomposed the salt, liberating chlorine and giving a deposit of the hydrated oxide. Strong nitric acid gave a precipitate, soluble on addition of water. Many of the heavy metals produced precipitates that remained insoluble on boiling, but dissolved on addition of a few drops of nitric acid.

#### RESULT OF ANALYSIS.

	Theory.	Found.		
$(\text{NH}_4)_2\text{O}$ .....	6.76	6.74	6.74	6.70
$\text{P}_2\text{O}_5$ .....	2.21	2.54	2.37	2.41
$\text{As}_2\text{O}_5$ .....	0.62	0.61	0.62	0.65
$\text{V}_2\text{O}_5$ .....	16.28	16.18	16.18	16.32
$\text{V}_2\text{O}_6$ .....	1.22	1.43	1.29	1.28
$\text{WO}_3$ .....	60.06	59.79	59.81	59.79
$\text{H}_2\text{O}$ .....	12.85	12.73	12.46	12.63
	100.00	100.02	99.47	99.78

There now remained only two more possibilities in these combinations:

*Ammonium phospho-arsenico-vanadico-tungstate, and*  
*Ammonium phosphorico-arsenico-vanadico-tungstate.*

They were prepared, but the crystals obtained were not well

defined, being also mixed with many impurities. After several attempts to get them, the work was given up. It seems very probable, however, that they can be obtained pure, and will be a subject for further study.

## CONCLUSION.

The formulas as given above cannot be looked upon as being definite. The writer is well aware that other views and interpretations may be given to his results, but as even these cannot be absolutely demonstrated, he regards the written formulas as wholly tentative. They will receive further study. They may be multiples of the same, or perhaps not so complicated as would appear. As there is no method, at present, to determine the molecular magnitude of such bodies, the only recourse was the result of analysis. It will be readily seen, that a slight error in the percentage of arsenic or phosphorus would alter the whole formula. It can only be claimed that such compounds exist, and that the constitution assigned to them remains open to correction.

UNIVERSITY OF PENNSYLVANIA.

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NOTES.

*Additional Note on Filtration of Crude Fiber.*—The method of filtering crude fiber described by Mr. Thatcher in the December Journal is one which, I believe, is practiced in a number of laboratories in this country. There is, however, one serious objection to this process. It frequently happens that it is desirable to make a chemical examination of the crude fiber and in such cases the method described by Mr. Thatcher would not answer at all, owing to the contamination of the material with asbestos.

A method eliminating all these difficulties is found in the use of a Büchner funnel, using well-fitting filters of hardened paper. These filters are perfectly resistant to the boiling acid and alkaline solutions. In the König method it is advisable to dilute the boiling glycerol-sulphuric acid with an equal volume of hot water before filtering. Using suction, the filtration is very rapid, owing to the large surface exposed. After washing the fiber with hot water, it is treated with a little alcohol and, after sucking as dry as possible, scraped or brushed from the paper into a weighing-

bottle, where it is dried and weighed. The fiber obtained in this way is in excellent condition for further examination (microscopic, ash, pentosans, cellulose, etc.). There is no danger of contamination with fiber from the hardened filters; in fact the latter may be re-used many times. C. A. BROWNE, JR.

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### NEW BOOKS.

NOTIONS FONDAMENTALES DE CHIMIE ORGANIQUE. PAR CH. MOUREAU, Professor agrégé à l'École supérieure de Pharmacie de l'Université de Paris. Paris: Gauthier-Villars. 1902. 286 pp.

This book may be useful under French conditions as a syllabus or memorandum in connection with a course of lectures on theoretical organic chemistry to mature students, but it is difficult to see in what way it can serve American teachers or American elementary students.

The book is clearly written but has grave faults in the selection and arrangement of material for a book intended for beginners. Its preface indicates that it is an introduction to organic chemistry. But elementary students could hardly avoid being overwhelmed by the first 60 pages which are devoted to an outline of theory which includes atoms, molecules, isomerism, valence, radicals, bonding, saturation and unsaturation, homology, nomenclature and the stereochemistry of carbon, nitrogen, and sulphur; and all this before a substance is described or its mode of occurrence or preparation are indicated. In a book of reference and if accompanied by original references, this outline would be admirable but in this place it seems excessive.

In the body of the book, substances are treated together which contain the same substituted radical, which have the same kind of functional activity. The treatment is clear and the classification has its advantages but it is questionable whether in an elementary book it is not better to take up first methane and its homologues and their derivatives, each class of which is made up of members so nearly alike that a full study of one is a nearly complete study of all, and then turn to the other hydrocarbons to study them and their derivatives by illustration and in the mass.

The absence, in the majority of cases, of any statement of the sources of substances which are found in nature is quite noticeable especially in a book written by a professor in a school of phar-

macy and so also is the absence of any indications of the industrial value of substances. It would have been more logical either to include more such material or else to omit the small amount now included.

It is perhaps hardly necessary to mention that the book has no alphabetical index, a time-saving device which seems to be appreciated by very few French writers. H. W. HILLYER.

AN INTRODUCTION TO CHEMISTRY. BY D. S. MACNAIR. London: George Bell & Sons. 1902. xii + 187 pp.

This is an admirable example of that class of text-books to which Professor Alexander Smith refers in his "Teaching of Chemistry in the Secondary School" under the heading of "The Nature Study Method." No reference is made to the atomic theory, but formulae and equations are freely used, being treated "solely as a short-hand expression of the proportions by weight in which the elements are found by experiment to combine." All but a few of the experiments (intended to be performed by the teacher) are within the capabilities of boys of fourteen or fifteen.

A. M. PATTERSON.

CHEMISTRY BY OBSERVATION, EXPERIMENT AND INDUCTION. A LABORATORY MANUAL FOR STUDENTS. BY J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York: John Wiley & Sons. 1902. 12mo., viii + 192 pp. Price, 75 cents.

This laboratory manual is divided into four parts: In the first part, consisting of 25 pages, there is a description of the commoner forms of laboratory appliances and some instruction in manipulation. The second part, 9 pages, contains instructions and questions on specific gravity, electrolysis, specific heat and the reduction of gas volumes to normal conditions. The third part, 8 pages, entitled "theoretical chemistry" deals with chemical and physical changes, elements and compounds, acids, bases and salts. The fourth part, 144 pages, is devoted to descriptive chemistry. The elements and compounds are prepared according to the directions given and the student's attention is called to the salient properties of the substances he has made by a number of questions. The book serves also as a laboratory note-book, as sufficient space is left in the text for the written answers to the questions. In the opinion of the reviewer the book would have been improved by the introduction of some accurate quantitative experiments illustrating some of the general laws of chemical combination. Also an

elementary exposition of the theories of solution, ionization, etc., would not have been out of place. EDWARD H. KEISER.

**A TEXT-BOOK OF QUANTITATIVE CHEMICAL ANALYSIS.** BY FRANK JULIAN. St. Paul, Minn.: The Ramsey Publishing Co. 1902. 604 pp. Price, \$6.00 net.

"This volume is intended for the aid of students who, having a fair acquaintance with the elements of general chemistry, can devote a limited time to quantitative analysis concurrent with or following the usual qualitative course; and as an introduction to the monographs on special departments of technical analysis....."

"In Part I, after outlining the general principles of the art, there are described the operations of solution, precipitation, etc., and the appliances commonly employed for the purposes." In Part II is found "a graded series of exercises chosen with a view to illustrate the leading principles in analysis....." In Part III technical analysis and special methods are considered. Part IV contains "Notes on the Methods of Analysis," while an appendix offers a discussion of "certain phases of the important subject of the practice of technical and industrial analysis."

This brief summary may serve, perhaps, to give an idea of the scope of the book. It seems hardly probable that it will be serviceable to students, who "can devote only a limited time to quantitative analysis," nor to "those who are content to remain permanently at routine analysis," but to young men who wish to become chemists, to more advanced students, who are anxious to broaden their horizon, and to the technical chemists, who have regard for something beyond their daily duties, it can not fail to be helpful.

Although it lacks, necessarily, the detail of special monographs or of extended works like those of Boeckman, Allen, and others, there is scarcely a similar book of moderate size, in which so many valuable suggestions can be found.

Among the topics treated with exceptional fulness are the following: Attributive Methods, Calculation of Analyses, Errors and Precautions, Colorimetry, Proximate Organic Analysis, Notes on the Methods of Analysis.

One may question the usefulness of this book as a laboratory guide, another may prefer a different selection of exercises for the illustration of the principles of analysis; others may hold opinions

contrary to those of the author, but none, I think, will fail to find it abounding in information, stimulating and tending to the advancement of the science and art of analysis. L. B. HALL.

**QUANTITATIVE CLASSIFICATION OF IGNEOUS ROCKS, BASED ON CHEMICAL AND MINERAL CHARACTERS.** BY WHITMAN CROSS, JOSEPH P. IDDIGS, LOUIS V. PIRSSON, HENRY S. WASHINGTON. With an Introductory Review of the Development of Systematic Petrography in the Nineteenth Century, by WHITMAN CROSS. Chicago: The University of Chicago Press. London: William Wesley & Son. 1903. 283 pp.

In this volume have been brought together the two essays under the above titles that appeared in Volume X of the *Journal of Geology* (see abstracts in this Journal, 24, R., 454, and 25, R., 7), with the addition of tables to aid in the calculation of the mineral and chemical compositions of rocks, and with a glossary of the new terms employed in the nomenclature. To adequately review this important work would require much space. It seems, therefore, only necessary to refer to the second of the above-mentioned abstracts, and to quote the following passages from the authors' preface.

"Much of the material will be useful to those, also, who do not follow the new classification, since it has a general application to petrography. Thus the 'Review of the Development of Systematic Petrography in the Nineteenth Century' presents a historical sketch of the subject which is valuable to all students of petrology."

"The methods of calculation by which the minerals of a rock may be reckoned from its chemical analysis, and the reverse process, will become more and more of a requirement in the practice of petrographers, as the demand for quantitative description increases. And the convenience of tables in carrying on the operation will be appreciated by all who undertake the work."

"The glossary will be found useful to those who adopt the new system in defining specifically each new term, particularly the magmatic names which appear for the most part only in the tables of the five classes where it requires some consideration to frame their definitions. Their full value will be appreciated when they are studied in connection with the collection of some thousands of rock analyses made within the past fifteen years, which has been prepared by Henry S. Washington, and will be published shortly."

"It is hoped that the present publication will contribute to the

better understanding of the development of petrography, and to a fuller appreciation of its defects and needs, and will point out a way along which substantial advancement may be made in the future."

W. F. HILLEBRAND.

ŒUVRES COMPLÈTES DE J.-C. GALISSARD DE MARIGNAC Tome I 1840-1860 Paris: Masson et Compagnie. Price, by subscription, 25 francs for the two volumes.

This is a beautiful volume of 8 + lv + 701 quarto pages. Fifty-five pages contain a well-balanced and admirable account of the life and scientific labors of the great Swiss chemist, written with affectionate and well-controlled enthusiasm by his son-in-law. Then follow the earlier half of his scientific papers, which appeared before the end of the year 1860. Thirty-eight are memoirs reporting his own work, and twelve are notes commenting on papers of other scientific men which were closely related to subjects treated in his own papers. The order is chronological, and the paging of the original memoirs is reproduced in the margin.

Marignac was born in Geneva in 1817, and was professor of chemistry there from 1841, as well as of mineralogy also from 1845, till failing health put an end to his teaching in 1878. For perhaps five years longer, he was able to accomplish something in a private laboratory at his house; afterwards, till his death in 1894, he retained his full intellectual powers, and endured with fortitude a good deal of suffering.

Four of his papers were undertaken under the direction of Liebig, and belong to organic chemistry. A few relate to mineralogy; Marignac enjoyed pedestrian tours among the Alps, from which he brought back minerals which he loved to investigate. One paper concerns the theory of the famous experiment of Foucault in which the rotation of the earth is demonstrated by the change of the plane of motion of a free pendulum. One concerns the properties of sulphuric acid, and one describes a hydraulic blowing engine used in Westphalia; Marignac was *Ingenieur des Mines*.

The remaining papers of the present volume are all the work of a great chemist of splendid manipulative skill who devoted the best efforts of his life to the determination of atomic weights. Many were the elements for which his results will always be an



important part of our material. He gave values for no less than twenty-eight elements besides gadolinium, and also accomplished much crystallographic work, suggested by Mitscherlich's law of isomorphism, and bearing upon the formulae of compounds of silicic, titanic, tungstic and other acids. The determination of the atomic weights of cerium, lanthanum, didymium, and other elements, led to studies of the rare earths. A considerable labor on the specific heats of solutions of certain salts was also suggested by his interest in atomic weights. The Royal Society's catalogue makes us eager to see the papers remaining for the second volume, now about due.

It is much to be desired that this impressive record of the great work of an eminent chemist be made easily accessible in the United States.

EDWARD W. MORLEY.

**A LABORATORY OUTLINE OF GENERAL CHEMISTRY.** BY ALEXANDER SMITH, B.Sc., PH.D., Associate Professor of Chemistry in the University of Chicago. Second edition, revised.

The reviewer has read this laboratory guide with interest and pleasure. It has appealed to him as a teacher, who has followed practically similar methods in the instruction of beginners for many years, and naturally the process of development and the examples in experimentation have proved very attractive. It is scarcely to be expected that exceptions would not be found to the array of experiments and the modes of procedure—every teacher will make some exceptions, for each one has his own favorite solution of the problems confronting him, as has Dr. Smith; otherwise this little volume probably would not have been prepared in the face of the numerous existing guides upon the same subject. But one doubt shall be mentioned. It is that the exercises here and there seem to call for knowledge and manipulative skill beyond that which the beginner, absolutely ignorant of chemistry, possesses, and upon whose mind the truths deduced will not make the lasting impression for which every teacher so fondly hopes. It strikes one as if the course, pursued as laid down, would be splendidly adapted to students who have some knowledge of the subject and whose purpose it is to obtain a well rounded-out course in general experimental chemistry. Perhaps by the judicious selection of experiments and a final general review, omitting nothing, the main object would be attained. However,

the little volume should be carefully studied. It will help many. It merits recognition and will receive it. It is the product of an earnest, wide-awake and thoughtful teacher who has performed his task with consummate skill—with lucidity in statement, accuracy in fact and care in detail; hence, it is most welcome.

EDGAR F. SMITH.

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### BIOCHEMISCHES CENTRALBLATT.

The great strides made in medical chemistry and in those fields of medicine verging on chemistry have necessitated the publication of a central organ. This is now published in Berlin by Carl Oppenheimer, under the direction of Ehrlich, Fischer, Kossel, Liebreich, Müller, Proskauer, Salkowski and Zunts, and they have appointed Heinrich Stern, of New York, editor for the United States and Canada. The object of the publication will be:

A—To report such experiments and observations of physical and applied chemistry as are of importance to the physician.

B—Reports on the physiology of plants.

C—Physiological chemistry in the narrower sense (constituents of the body and their derivatives).

D—Chemistry of the tissues and organs under normal and pathological conditions.

E—Chemistry of digestion, secretions and excretions, metabolism and blood.

F—Ferments and fermentation; toxins of a non-bacterial nature.

G—Chemistry of the pathogenic micro-organisms (toxins, anti-toxins), phenomena of immunity.

H—Toxicology and pharmacology.

I—Hygienic chemistry, disinfection, examination of water.

As this is the only international organ devoted to these scientific fields, American observers and investigators will find it to their interests to prepare abstracts of their papers which have appeared since January 1st and will appear hereafter, and send them to Heinrich Stern, 56 East 76th Street, New York City.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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[CONTRIBUTION FROM THE LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION.]

### NITROGEN IN PROTEIN BODIES.

BY THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received February 9, 1902.

To properly differentiate and classify the protein bodies it is necessary to employ some method based on the structure of their molecules. Many of the color reactions, it is true, give us evidence of certain complexes in the protein molecule, but most of these reactions are characteristic of the protein bodies in general, and in but few cases distinguish between individual proteins. Furthermore, these reactions give no quantitative measure of the different complexes which cause them, and in these quantitative relations lies one of the most important differences between the several protein bodies. Until recently, knowledge regarding the structure of the protein molecule has been chiefly obtained by detailed study of the decomposition products resulting from boiling the protein with strong acids. A quantitative determination is possible for only a few of these decomposition products and, as large quantities of pure material and much time and skill are required for the examination, investigations of this kind have been applied to only a few of the known proteins.

Kossel and Kutscher<sup>1</sup> have recently perfected their method for

<sup>1</sup> *Ztschr. physiol. Chem.*, 31, 165 (1900).

determining the basic bodies, histidin, arginin and lysin, three of the most important decomposition products yet obtained from proteins. From their results, it would appear that one of the best means at present available for distinguishing between the several proteins lies in a determination of the proportion of these bases which they contain. We have accordingly tried to determine the proportion of the different classes of nitrogenous decomposition products yielded by several of the proteins previously prepared and studied in this laboratory but as, in many cases, only small amounts were available, it is not at present possible to apply Kossel and Kutscher's method to them all.

As preliminary to a more exact study of our preparations, we have used a method proposed by Hausmann<sup>1</sup> for determining the proportion of nitrogen in different forms of combination that occur among the decomposition products which result after boiling the protein for a long time with acids. Although this method has been subjected to very severe adverse criticism, we have found that, under suitable conditions, it yields fairly uniform results and affords a rapid means for approximately determining the relations of different preparations to one another. Thus we have found by its use that some of our preparations from different seeds which were so nearly alike in composition and reactions that no difference could be detected between them sufficient to warrant the conclusion that they were not the same chemical individual, yield such different proportions of nitrogen in the several forms of binding that there can be no longer any doubt that they are distinctly different substances. On the other hand, many preparations of different origin which we have heretofore considered to be identical, have yielded the same proportion of the different forms of nitrogen and consequently our former opinion respecting the identity of these protein preparations is very greatly strengthened. We do not assert that Hausmann's method is capable of yielding accurate results respecting the true proportion of nitrogen in the various forms of binding, but that it yields valuable comparative results under the conditions which we have employed, is evident from an examination of our determinations given in the following pages.

Hausmann's method consists in boiling the protein with strong hydrochloric acid until it is completely decomposed and then de-

<sup>1</sup> *Ztschr. physiol. Chem.*, 27, 92 (1899).

termining: (1) The nitrogen which can be expelled from the solution as ammonia by distillation with magnesia; (2) that which is precipitated by phosphotungstic acid from the solution thus freed from ammonia; and (3) the nitrogen remaining in the filtrate from the phosphotungstic acid precipitate. In this way Hausmann thought the amide nitrogen (1), the diamino-nitrogen (2), and the remaining nitrogen (3), belonging almost wholly to monamino acids, might be quantitatively determined. This method has, however, received, such severe criticism that it has found but little application and the results obtained by it have been accorded but slight consideration.<sup>1</sup>

Hausmann supposed that the amount of amide nitrogen was quite accurately determined by his method and was characteristic for each proteid, but Henderson<sup>2</sup> soon showed that the amount of ammonia obtained depended on the strength of the acid used in decomposing the proteid and on the time of boiling.

Schulze and Winterstein<sup>3</sup> found that after precipitating the solution of the decomposition products of proteins with phosphotungstic acid, a small amount of ammonia could be obtained from the filtered solution by distilling with magnesia. In agreement with this observation, Hart<sup>4</sup> found that a somewhat greater proportion of ammonia was obtained by distilling the solution of the decomposition products with magnesia than with barium carbonate. From these facts it would appear that distillation with magnesia does not give an accurate measure of the amide nitrogen yielded by the protein.

Kutscher<sup>5</sup> next stated that, according to experiments by Gulewitsch, the phosphotungstic acid compound of arginine is notably soluble in water; that the phosphotungstic acid precipitate of the diamino acids is soluble in a sufficient excess of the precipitant; that in the mixture of acids obtained by boiling the protein with hydrochloric acid an immediate precipitate results on adding phosphotungstic acid, but that, on increasing the amount of the latter, a further precipitate appears after a time and that

<sup>1</sup> Hofmeister ("Ergebnisse der Physiologie," Vol. I, p. 778 (1902)), in whose laboratory Hausmann's work was done, says that more accurate estimations by Hausmann's process will soon be published by Th. Gümbel, and the objections raised against this method by Kutscher and others will be met.

<sup>2</sup> *Ztschr. physiol. Chem.*, 29, 47 (1900).

<sup>3</sup> *Ibid.*, 22, 563 (1901).

<sup>4</sup> *Ibid.*, 22, 347 (1901).

<sup>5</sup> *Ibid.*, 31, 215 (1900).

this time gradually becomes longer after each addition of the acid. This latter precipitate is crystalline, is soluble in water, dilute acids, and in acidified dilute phosphotungstic acid solution, and does not contain diamino acids.

Kutscher conducted experiments with Hausmann's method in which he employed different volumes and proportions of phosphotungstic acid for precipitating the diamino acids obtained from casein, the results of which, under the different conditions employed, varied materially from one another and very greatly from that obtained by Hausmann with the same protein. Nevertheless, two results, secured under the same conditions, agreed very closely. Kutscher concluded that Hausmann's method cannot yield useful results.

Wetzel<sup>1</sup> employed Hausmann's method with gelatin, conchiolin and silk glutin. He found the same amount of nitrogen, as ammonia, in gelatin as did Hausmann, but only one-half as much diamino nitrogen. He explains the difference by saying "The amount of nitrogen which is obtained is too low for dilute solutions, too high for very concentrated, since in the one case all the bases are not precipitated and in the other, besides the bases, probably amido acids are also precipitated."

Chittenden and Eustis<sup>2</sup> state that the amount of bases precipitated by phosphotungstic acid from solutions containing the decomposition products of the proteins is variable and cannot be taken as a quantitative measure of the same.

Schulze and Winterstein<sup>3</sup> next determined the amount of histidine, arginine and lysine which they were able to isolate from the decomposition products of several crude preparations of vegetable proteins, and found that the amount of nitrogen contained in these bases fell considerably below that precipitated by phosphotungstic acid, according to Hausmann's method. From this they conclude that phosphotungstic acid precipitates other decomposition products than the three determined.

Schulze and Winterstein<sup>4</sup> next studied the deportment of some monamino acids towards phosphotungstic acid and found that neither glycocol, optically active and inactive leucine, amino-valerianic acid or tyrosine were precipitated from their 5 per cent.

<sup>1</sup> *Ztschr. physiol. Chem.*, 29, 403 (1900).

<sup>2</sup> *Am. J. Physiol.*, 3, 31 (1900).

<sup>3</sup> *Ztschr. physiol. Chem.*, 33, 547 (1901).

<sup>4</sup> *Ibid.*, 33, 574 (1901).

solutions by phosphotungstic acid, but that of phenylalanine under these conditions gave an oily precipitate which, after a time, became crystalline. About 50 cc. of cold water were required to dissolve the precipitate produced by 0.1 gram of this substance.

Whether phenylalanine is thrown down by phosphotungstic acid from solutions containing the decomposition products of proteins, depends on the concentration of the solution. Since this body has as yet been found only in small quantity among protein decomposition products, it may escape precipitation, but the known tendency of substances to separate together from solution may cause it to precipitate to a greater or less extent.

Although a careful examination of the phosphotungstic acid precipitates failed to reveal the presence of monamino acids, even when methods were used which would surely have shown the presence of even small amounts of leucine and tyrosine, they conclude that it is probable that monamino acids are, in fact, carried down with the phosphotungstic acid precipitate.

From the preceding statements, it is evident that Hausmann's method, as he defined it, cannot be used to determine accurately the proportion of amido-, diamino- and monamino-nitrogen in the decomposition products of the various proteins. It is possible, however, under suitable conditions, to obtain valuable *comparative* results by its use, whereby differences between the various proteins are made plainly evident.

Henderson's statement that the amount of ammonia obtained depends on the strength of acid with which the proteid is boiled, as well as on the time of boiling, is doubtless correct, but an examination of his determinations, made under different conditions, shows that it is necessary to much increase the strength of the acid or greatly prolong the boiling in order to materially affect the result. It is therefore possible, under similar conditions, to obtain a uniform proportion of ammonia by distilling with magnesia. That *all* the ammonia, thus obtained, is derived from ammonium salts formed by the action of the boiling acid on amides is improbable, in view of Schulze and Winterstein's observation and also that of Hart.

We have, in the following investigation, determined the ammonia yielded by various preparations of the same protein on distillation with magnesia, and have, as inspection of the figures given in the following pages shows, obtained such uniform results that

they afford a ready means for comparing supposedly identical proteins.

Whether Hausmann's method can be modified so that the results will show the true proportion of basic nitrogen yielded by the proteins, will require more extended investigations than have as yet been undertaken. It will be shown later in this paper that, under the conditions which we have employed, the amount of basic nitrogen precipitated by phosphotungstic acid corresponds pretty closely with that contained in the histidine, arginine and lysine which Kossel and Kutscher<sup>1</sup> found in several proteins from cereal grains, but falling, as would be expected from the known slight solubility of arginine phosphotungstate, a little below them.

Unfortunately, these investigators did not examine any of the proteins yielding large amounts of basic nitrogen, except histone, and we have at present no accurate knowledge of the proportion of arginine, histidine and lysine which any of these contain. The determinations made by Schulze and Winterstein show that edestin and conglutin contain large proportions of these diamino-acids, but they did not employ pure conglutin and their determinations were made by Kossel's older method which, supposedly, does not yield such reliable results as the later one, recently devised by Kossel and Kutscher. Furthermore, we have no evidence that these three diamino acids are the only basic decomposition products of proteins and it may well be that further investigation will reveal the presence of others in some of the vegetable proteins, especially those rich in nitrogen.

Kutscher lays much stress on the solubility of the phosphotungstic acid precipitate, but our experience has not led us to consider that it is soluble to such an extent as he would have us believe. When the phosphotungstic acid precipitate separates in abundance, we have frequently noticed that it forms a relatively stiff jelly which, on stirring, diminishes greatly in volume and after a time becomes partly crystalline, as shown by the microscope. The same phenomenon, though less marked, usually occurs on washing, the precipitate diminishing in volume and becoming more crystalline, but not, so far as we have observed, dissolving to a noticeable extent.

That the amount of nitrogen precipitated by phosphotungstic acid varies with the conditions, is evident from the facts brought

<sup>1</sup> *Ztschr. physiol. Chem.*, 31, 165 (1900).



forward by Kutscher, who, however, worked under extreme conditions, his solutions being very concentrated and the amount of phosphotungstic acid very large, so that coprecipitation of the monamino acids might be expected.

To determine the best way of employing Hausmann's method, we have tried the following experiments with a very pure preparation of crystallized edestin from the hemp seed:

I. One gram of the air-dry crystals of edestin was boiled for about seven hours with 12 per cent. hydrochloric acid, the solution evaporated to a small volume in order to remove most of the excess of hydrochloric acid, diluted with water, distilled with magnesia and the ammonia determined. The residual solution was then filtered, concentrated to approximately 100 cc., 5 grams of sulphuric acid added and then, after cooling, a solution of phosphotungstic acid of unknown strength, until no further precipitation occurred at once on adding more of the reagent to the clear solution above the precipitate. After twenty-four hours, the precipitate was filtered out and washed with a dilute solution of phosphotungstic acid containing some sulphuric acid. Nitrogen was then determined in the precipitate together with the filter.

II. One gram of the same preparation of edestin was dissolved in dilute hydrochloric acid, somewhat more than an equal volume of concentrated acid added and the solution boiled with a reflux condenser for seven hours. After boiling a short time, the excess of hydrochloric acid passed out of the condenser so that the solution soon came to contain about 20 per cent. of the acid. The solution was then treated like I, and the nitrogen determined in the residue, filtered out after distilling off the ammonia. The filtered solution was then concentrated to 100 cc., 3 cc. of concentrated sulphuric acid added and, after cooling to about 20°, a solution containing 20 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 cc. was added, 1 or 2 cc. at a time, as long as an immediate precipitate formed in the solution cleared by subsidence. For this purpose, 15 cc. of the phosphotungstic acid solution were required. After standing half an hour, this precipitate was filtered out and 15 cc. more phosphotungstic acid were added. The solution remained clear for a few seconds and then slowly yielded a second voluminous precipitate which the microscope showed to consist of spherical aggregates of narrow crystalline plates together with amorphous matter entangled in a

very voluminous jelly. No noticeable difference existed in the appearance of this precipitate and that first thrown down. On stirring, the voluminous precipitate, which at first filled nearly the whole of the solution, settled rapidly to a slight crystalline deposit. After standing several hours, the clear solution was decanted and 35 cc. more of the phosphotungstic acid solution were added. After standing over night, a mere trace only of the precipitate separated from this last solution. The two precipitates first formed were washed with a solution containing 2.5 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 cc. and nitrogen determined in them.

III. One gram of the edestin crystals was treated in the same way as II, except that after adding the first 15 cc. of phosphotungstic acid the solution was allowed to stand twenty-four hours before filtering, no more phosphotungstic acid being added.

IV. One gram of the edestin was treated like III, except that 30 cc. of the phosphotungstic acid were used. The filtrate from the precipitate thus produced was made up to 500 cc, and nitrogen determined in 100 cc. of it.

V. One gram of the edestin was treated like III except that 60 cc. of the phosphotungstic acid were added.

The results of these determinations in per cent. of the edestin dried at 110° were the following:

	I.	II.	III.	IV.	V.
Phosphotungstic acid added..	? cc.	15 cc. + 15 cc.	15 cc.	30 cc.	60 cc.
Nitrogen as ammonia .....	1.93	1.86	1.86	1.86	1.86
Basic nitrogen .....	5.68	{ 5.05 0.70	5.39	5.98	6.06
Non-basic nitrogen .....	10.23	...	...	10.01	...
Nitrogen in magnesium oxide precipitate .....	...	0.11	0.11	0.13	0.11
	<hr/> 17.94			<hr/> 17.98	

These figures show that the amount of ammonia formed is very uniform, even though the strength of the acid varies considerably,—from 12 to 20 per cent. The amount of basic nitrogen found in III shows that 15 cc. of the phosphotungstic acid is not enough, a result confirmed by the figures under II, where the addition of 15 cc. more phosphotungstic acid to the filtrate from the precipitate produced by the first 15 cc. yielded a second precipitate containing 0.7 per cent. more nitrogen. As 60 cc. of

phosphotungstic acid in V gave the same result as 30 cc. in IV, it would appear that the latter quantity was sufficient for complete precipitation and that a considerable excess of the precipitant has no solvent action, as might have been expected from Kutscher's statements.

The sum of the different forms of nitrogen falls considerably below the total nitrogen contained in edestin, namely, 18.64 per cent. This deficiency probably falls, for the most part, on the non-basic nitrogen, as it is difficult to determine this with accuracy, because only one-fifth of the solution can be employed and consequently all errors arising from incomplete oxidation during digestion with sulphuric acid are multiplied by five. Owing to the large amount of phosphotungstic acid present, larger quantities of the solution cannot well be used, and even with one-fifth, the solution bumps so badly, on boiling with sulphuric acid, that it is very difficult to effect complete conversion of the nitrogen into ammonia. It is better, therefore, to omit this determination and find the amount of non-basic nitrogen by difference.

It is evident from the results of these comparative determinations that a considerable latitude in the conditions may occur without noticeably affecting the result, so that uniform results may be obtained by using Hausmann's method under suitably defined conditions.

The method which we have adopted is the following: About 1 gram of the protein is boiled with 20 per cent. hydrochloric acid until the solution no longer gives the biuret reaction, usually from seven to ten hours. It is then evaporated on the water-bath to 2-3 cc. and the bulk of the free hydrochloric acid thus removed. The residual solution is transferred to a flask with about 350 cc. of water, and a cream of magnesia which has been freed from every trace of ammonia by long boiling is added until in slight, but distinct excess. After distilling and determining the ammonia, the solution in the flask is filtered through nitrogen-free paper and the residue, thus collected, washed thoroughly with water, and nitrogen determined in it, together with the paper, by Kjeldahl's method. The filtered solution is next concentrated to 100 cc., cooled to 20°, 5 grams of sulphuric acid added, and then 30 cc. of a solution containing 20 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 cc. After twenty-four hours, the precipitate is filtered out and washed with a solution containing

2.5 grams of phosphotungstic acid and 5 grams of sulphuric acid per 100 cc. The washing is effected by rinsing the precipitate from the filter into a beaker and returning to the paper three successive times, each portion of the wash-solution being allowed to run out completely before the next is applied. About 200 cc. of washings are thus obtained.<sup>1</sup>

The nitrogen contained in the precipitate is then determined by transferring it to a flask of Jena glass holding 600 cc. and digesting with 35 cc. of sulphuric acid for seven or eight hours. During the digestion, potassium permanganate crystals are added three or four times. In the few cases, where the phosphotungstic acid precipitate is small, less sulphuric acid is used, enough being taken in each case to prevent too violent bumping. The remaining nitrogen, belonging chiefly to monamino acids, is found by subtracting the sum of the nitrogen found in the preceding operations from the total nitrogen contained in the protein under examination.

#### THE BINDING OF NITROGEN IN VARIOUS PURE PROTEINS.

In studying the amount of furfural yielded by various protein substances when distilled with 12 per cent. hydrochloric acid, we obtained solutions containing their decomposition products in which we determined the proportion of the different groups of nitrogen compounds in the same way as described in Experiment I with edestin. In the following pages these results are marked *a*.

We later studied Hausmann's method more carefully and, after trying the experiments already described, adopted the method just given. The results thus obtained are marked *b*.

In nearly all of these proteins we determined the amount of non-basic nitrogen directly, but as in many cases the sum of the nitrogen in the several groups of compounds fell below the total contained in the preparation, we give in the following pages the amount found by difference, which we consider to be more nearly correct than that found by direct determination.

#### *Edestin.*

The name edestin was first applied to the globulin obtained by

<sup>1</sup> Hausmann directed that the washing be continued until the fluid ran out colorless, but in all the solutions which we precipitated with phosphotungstic acid there was either no coloring-matter at all or so little that the solution was, at the most, only a pale straw color. This was probably due to precipitation of humus by magnesia.

the writer from several different seeds<sup>1</sup> and in this paper he says that "this substance (the globulin of the cotton seed) agrees in composition with the vitellin which exists in the seeds of wheat, maize, hemp, castor bean, squash and flax. As the properties of the preparations obtained from all these sources are substantially alike, there can be little doubt that one and the same proteid exists in them all. For this body we adopt the name *edestin*, from the Greek *edestos*, signifying edible, in view of its occurrence in so many important food-stuffs."

In an earlier paper on "Crystallized Vegetable Proteids"<sup>2</sup> the writer compared the crystallized globulins from the hemp seed, castor bean, flax seed and squash seed and showed that in crystalline form, composition and reactions the various preparations were practically alike. In conclusion he stated: "It is impossible to assert that these four globulins are the same, but, since differences exist between different preparations of globulin from the same seed as great as those found among the globulins of these different seeds, the writer is disposed to consider these four globulins as identical."

As it has since been found that most of the differences above referred to are caused by different minute proportions of combined acid,<sup>3</sup> whereby different salts of the protein were formed, it seemed even more probable that these four globulins were one and the same substance.

In another paper by Osborne and Campbell<sup>4</sup> the supposition was advanced, based on analyses by Chittenden, that the globulin of the cocoanut, which is obtained in crystals, is probably *edestin*.

In a paper on the proteids of the sunflower seed, Osborne and Campbell<sup>5</sup> state that "it is therefore our opinion that the sunflower seed contains, as its principal proteid, the globulin *edestin*, but that, as obtained by extraction from the seed, this is mixed with helianthotannic acid, from which we have not succeeded in separating it completely."

We have now determined the different forms of nitrogen in such of these preparations as are at present available, with the following results:

<sup>1</sup> Report Conn. Agr. Expt. Station for 1893 and this Journal, 16, 778 (1894).

<sup>2</sup> *Am. Chem. J.*, 14, 662 (1892).

<sup>3</sup> Report of Conn. Agr. Expt. Sta. for 1896, p. 369, and this Journal, 19, 482 (1897); also this Journal, 21, 486 (1899) and Report Conn. Agr. Expt. Sta. for 1900, p. 399.

<sup>4</sup> Report Conn. Agr. Expt. Sta. for 1895, p. 288, and this Journal, 18, 609.

<sup>5</sup> Report Conn. Agr. Expt. Sta. for 1896, p. 374, and this Journal, 19, 487.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN PROTEINS  
HERETOFORE SUPPOSED TO BE EDESTIN.

Source.		Nitrogen as NH <sub>4</sub> .	Basic nitrogen.	Non-basic nitro- gen.	Nitrogen in mag- nesium oxide precipitate.	Total nitrogen.
Hemp seed ( <i>Cannabis sativa</i> ).... {	a	1.93	5.68	11.04	...	18.64
	b	1.86	5.98	10.68	0.13	....
	c	1.86	6.06	10.62	0.11	....
Cotton seed ( <i>Gossypium herba- cium</i> ) .....	a	1.92	5.71	11.01	...	18.64
Cocoanut ( <i>Cocos nucifera</i> )..... {	a	1.34	6.02	11.05	0.07	18.48
	b	1.38	6.11	10.79	0.20	....
Castor bean ( <i>Ricinus communis</i> ). {	a	1.96	5.64	11.03	0.12	18.75
	I <sup>1</sup> a	2.06	4.77	11.60	0.05	18.48
	II b	1.89	4.68	11.64	0.27	....
Flax seed ( <i>Linum usitatissimum</i> ) {	III b	1.97	4.63	11.64	0.17	....
	IV b	2.04	5.15	10.88	0.33	....
	V b	2.04	4.56	11.66	0.22	....
	VI b	2.00	4.86	11.37	0.25	....
	I b	1.36	5.93	11.04	0.18	18.51
Squash seed ( <i>Cucurbita maxima</i> ) {	II b	1.21	6.04	11.01	0.25	....
	III b	1.26	5.94	11.08	0.23	....
	a	2.55	4.33	11.46	0.24	18.58
Sunflower seed ( <i>Helianthus an- nus</i> )..... {	b	2.58	4.21	11.55	0.24	....
	I, b	1.49	6.66	10.04	0.20	18.39
Wheat kernel ( <i>Triticum vulgare</i> ) {	II b	1.35	7.01	9.60	0.35	....

These figures show that the globulins from hemp seed, cotton seed and castor beans contain practically the same proportion of nitrogen in each of the different forms; that the globulins of the cocoanut and squash seed are very nearly alike but contain so much less nitrogen as ammonia than the globulins of the three seeds first named that there can be no doubt that they are distinctly different proteins; that the globulin of the flax seed and that from the sunflower seed contain very much less basic nitrogen than the others, but that the former is distinguished from the latter in yielding 0.5 per cent. less nitrogen as ammonia. The globulin from wheat is characterized by containing by far the largest proportion of basic nitrogen of any of these globulins and far more than any of the other proteins described in the following pages.

<sup>1</sup> All sets of figures used in this paper which are marked with Roman numerals were obtained from different preparations; those showing more than one determination on the same preparation are included in brackets.

We have not been able to determine the proportion of the different forms of nitrogen in the globulins of seeds of rye, barley and maize, which are very similar in properties and composition to that of wheat, and can therefore assert nothing as to the relations of these apparently identical proteins.

The facts here presented raise the question as to which of the above proteins should now be called edestin. Although the writer first applied the name *edestin* to the globulin of the cotton seed together with that "which exists in the seeds of wheat, maize, hemp, castor bean, squash and flax" he always considered that the crystallized globulin from the four seeds last named best represented this substance. We now find that only the globulins of hemp seed, castor bean and cotton seed are alike in respect to the proportion of their several nitrogenous decomposition products. In another paper we show that the globulin from cotton seed gives a strong Molisch reaction while those from the hemp seed and castor bean give none at all. We have then only two of the above globulins, with the possible exception of those of wheat and maize, which can still be considered alike, namely those from the hemp seed and castor bean. It seems best, therefore, to retain the name edestin for the globulin of these latter seeds, especially as it is now very generally applied to that from hemp seed. Whether the globulins from these two seeds are in fact alike is rendered doubtful by the other results of this investigation, for only those proteins appear to be identical that originate from seeds which are closely related botanically, *e. g.*, legumin from the pea, horse bean, lentil and vetch, vicilin from the pea, horse bean and lentil, gliadin from wheat and rye, and phaseolin from the kidney bean and adzuki bean.

### *Legumin.*

In the seeds of the pea, lentil, horse bean and vetch, Osborne and Campbell<sup>1</sup> studied the protein substance legumin, which, so far as a rigid comparison of the properties and composition of preparations from each of these seeds could show, appeared to be one and the same protein. A determination of the different forms of nitrogen in legumin from these four seeds has given the following results.

<sup>1</sup> Report of the Conn. Agr. Expt. Sta. for 1897, pp. 324, 337, 393, 361, and this Journal, 20, 348, 362, 393, 406 and 419.

## PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN LEGUMIN.

Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Pea ( <i>Pisum sativum</i> ) .....	$\left\{ \begin{array}{l} b \\ b \end{array} \right.$	1.66	5.24	10.74	0.27	17.91
		1.72	5.43	10.56	0.20	....
Lentil ( <i>Ervum lens</i> ).....	<i>b</i>	1.69	5.16	11.03	0.11	17.99
Horse bean ( <i>Vicia faba</i> ).....	<i>b</i>	1.62	4.92	11.34	0.11	17.99
Vetch ( <i>Vicia sativa</i> ) .....	<i>b</i>	1.75	5.17	10.90	0.18	18.00

In view of these results, and the fact that legumin from each of these seeds has the same composition and reactions, there can be little doubt as to the identity of the several preparations.

*Phaseolin.*

The writer has found that the chief protein in the seeds of the kidney bean is a globulin, to which he gave the name phaseolin.<sup>1</sup> Later Osborne and Campbell found<sup>2</sup> in the Japanese adzuki bean a globulin which was so like phaseolin, both in properties and composition, that it was stated to be that protein. They also found in the soy bean<sup>3</sup> a protein similar in properties and composition to phaseolin, in regard to which they say, "The soy bean meal contains a more soluble globulin which resembles phaseolin in composition and, so far as we could ascertain, also in its reactions. The amount of this protein is small and the evidence that it is in reality phaseolin is not wholly satisfactory."

The following table contains the determinations of the different forms of nitrogen yielded by a number of fractional precipitates of phaseolin from the kidney and adzuki beans and also by preparation 10 from the soy bean.

<sup>1</sup> Report Conn. Agr. Expt. Sta. for 1893, p. 186, and this Journal, 16, 633, 703 and 757.

<sup>2</sup> Report Conn. Agr. Expt. Sta. for 1896, p. 387, and this Journal, 19, 509.

<sup>3</sup> Report Conn. Agr. Expt. Sta. for 1897, p. 374, and this Journal, 20, 419.



## PERCENTAGE OF NITROGEN IN THE DIFFERENT FORMS IN PHASEOLIN.

Source.			Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Kidney bean ( <i>Phaseolus vulgaris</i> )	I	b	1.63	3.65	10.54	0.38	16.20
		a	1.74	3.48	....	...	....
	II	b	1.77	3.85	10.29	0.29	....
		b	1.63	3.51	10.74	0.32	....
	III	b	1.72	...	....	..	....
		b	1.69	4.32	9.99	0.20	...
Adzuki bean ( <i>Phaseolus radiatus</i> )	I	b	1.78	...	....	0.38	....
		b	1.69	4.10	10.15	0.26	....
	II	b	1.75	4.19	9.82	0.44	....
		b	1.77	4.24	10.03	0.16	....
	III	b	1.70	...	....	0.30	....
		b	1.69	4.17	10.16	0.18	....
	IV	b	1.76	4.11	10.05	0.28	....
		b	1.86	4.13	....	...	....
	V	b	1.78	3.83	10.22	0.37	....
		b	1.97	4.02	9.99	0.22	....
Soy bean ( <i>Glycine hispida</i> ).....	10	b	1.78	3.83	10.22	0.37	....
		b	1.97	4.02	9.99	0.22	....

Although the amount of basic nitrogen found in the phaseolin from the adzuki bean is distinctly and uniformly more than in that from the kidney bean, we are not inclined to consider the difference, which hardly exceeds the error of analysis, to be sufficient to warrant the conclusion that the globulins from these two seeds are different substances, especially as no other difference of any sort has been found between them.

*Legumelin.*

In most of the leguminous seeds which have been examined in this laboratory, a protein has been found which is soluble in exceedingly dilute saline solutions, is coagulated at about 60° and is obtained by dialyzing in alcohol the solutions previously freed from globulin by dialysis in water. It is thus separated in a coagulated form and can be freed from proteoses and other soluble, contaminating substances by washing with water. The properties, composition and occurrence of legumelin are given in a paper by Osborne and Campbell.<sup>1</sup>

The proportion of the different forms of nitrogen in legumelin is given in the following table, the designations of the prepara-

<sup>1</sup> Report Conn. Agr. Expt. Sta. for 1897, p. 365, and this Journal, 22, 410.

tions being those of products whose analyses were given under the same numbers in the papers already referred to.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN LEGUMELIN.

Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Pea ( <i>Pisum sativum</i> )	41 { 42 { 75 { 50 { 66 { 96 { 6 {	1.04 1.02 1.04 1.04 1.10 1.11 0.96 0.96 1.09	... 3.75 4.05 3.69 3.38 3.70 3.42 3.94 3.74	... 10.87 10.84 10.88 11.18 10.93 11.10 10.89 10.97	... 0.48 0.23 0.45 0.30 0.51 0.44 0.31 0.30	... 16.12 16.21 16.06 15.96 16.25 15.92 16.10 ...

All these preparations are characterized by yielding a decidedly smaller proportion of nitrogen as ammonia than any of the other proteins examined, with the exception of leucosin, which will next be discussed. The results obtained agree fairly with one another and make it highly probable that legumelin from the several seeds is one and the same protein substance.

*Leucosin.*

In the seeds of wheat, rye and barley there is found a small quantity of a protein having the properties of an albumin, being soluble in water and coagulable by heat at 52°.¹ In the wheat kernel the leucosin is contained chiefly in the embryo, of which it forms about 10 per cent.,² while in the whole wheat, including the embryo, only about 0.3 or 0.4 per cent. is present.

The proportion of the different forms of nitrogen in leucosin were found to be as follows:

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN LEUCOSIN.

Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Wheat ( <i>Triticum vulgare</i> )	I { II { III {	1.18 1.15 1.16	3.58 3.45 3.48	11.76 11.75 11.99	0.41 0.58 0.30	16.93 ... ...

¹ Osborne and Voorhees: *Am. Chem. J.*, 18, 392 (1893); Osborne: Report Conn. Agr. Expt. Sta. for 1894, p. 147; this Journal, 17, 429 (1895); Osborne: Report Conn. Agr. Expt. Sta. for 1894, p. 165; this Journal, 17, 539 (1895).

² Osborne and Campbell: Report Conn. Agr. Expt. Sta. for 1899, p. 305.

These results are similar to those obtained for legumelin, with which protein leucosin agrees closely in composition, reactions and temperature of coagulation. Leucosin yields the smallest proportion of basic nitrogen of any of the proteins examined except glutenin and the alcohol-soluble proteins.

### *Vicilin.*

In the seeds of the pea, lentil and horse bean there is a considerable quantity of a globulin associated with legumin, which is characterized by containing an extremely small proportion of sulphur. The properties of vicilin are given in a paper by Osborne and Campbell<sup>1</sup> and the proportion of nitrogen in different groups in the following table:

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN VICILIN.

Source.		Nitrogen as am- monia.	Basic nitrogen.	Non-basic nitro- gen.	Nitrogen in mag- nesium oxide precipitate.	Total nitrogen.
Horse bean ( <i>Vicia faba</i> ) ....	<i>b</i>	1.93	4.53	10.35	0.23	17.04
Lentil ( <i>Ervum lens</i> ) .....	<i>b</i>	1.75	4.59	10.77	0.13	17.24
Pea ( <i>Pisum sativum</i> ) .....	<i>b</i>	1.67	5.12	10.00	0.26	17.05

These results, while not in quite as close agreement as most of our others, are, in our opinion, near enough to one another to warrant the conclusion that the preparations from the different seeds are identical. The higher result for basic nitrogen in vicilin from the pea is, perhaps, due to the fact that 1.5 grams, instead of 1 gram, was used by mistake, and of the horse bean and lentil vicilin only 0.75 gram of each was available for the determination. Unfortunately, no more of these preparations is left, so that the determinations cannot now be repeated.

### *Conglutin.*

In the blue and yellow lupine, Osborne and Campbell<sup>2</sup> found globulin, in large proportion, which could be separated, by fractional precipitation, into two parts of different composition. The differences between the extreme fractions, in the case of the blue lupine, were only slight, suggesting the admixture or combination of some other substance. The differences between the extreme

<sup>1</sup> Report Conn. Agr. Exp. Sta. for 1897, p. 365, and this Journal, 20, 410.

<sup>2</sup> Report Conn. Agr. Expt. Sta. for 1896, p. 342, and this Journal, 19, 454.

fractions from the yellow lupine were, however, so considerable that it was a question whether or not two different proteins were present in this seed. The least soluble fractions of the globulin from the yellow lupine agreed in composition and reactions closely with the corresponding fractions from the blue lupine and were designated *conglutin*. The most soluble fractions differed in reactions and composition, especially in sulphur content, those from the yellow lupine containing more than three times as much sulphur as those from the blue lupine. The results of that investigation indicated that some organic substance, rich in sulphur, was present in these seeds, much more in the yellow than in the blue lupine, which combined with the conglutin and could be separated only with difficulty. It was, however, found<sup>1</sup> that on treatment with hot alkaline solutions the same proportion of sulphur was split off as sulphide from the preparations rich in sulphur as from those poor in this element. As it seemed improbable that a contaminating sulphur-containing substance should contain the same proportion of sulphur convertible into sulphide as did the protein, it became a question whether or not there were two different proteins present. Hoping that we might get some evidence bearing on this point, we have determined the proportion of nitrogen in the different groups in several preparations from these seeds, with the following results, the designations of the preparations being the numbers of the preparations described in the papers referred to.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN CONGLUTIN.

Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Blue lupine ( <i>Lupinus angustifolius</i> ) .....	37 a	2.12	5.52	10.21	0.09	17.94
	2 a	2.18	5.25	10.36	0.05	17.84
	23 {	2.14	4.90	10.65	0.24	17.93
	b	2.00	5.06	10.65	0.22	....
Yellow lupine ( <i>Lupinus luteus</i> ) .....	26 b	2.22	5.24	10.10	0.24	17.80
	28 + 29 b	2.04	5.20	10.27	0.27	17.78
	30 + 31 + 32 {	2.68	5.20	10.30	0.03	18.21
	b	2.61	5.06	10.29	0.25	....

<sup>1</sup> Report Conn. Agr. Expt. Sta. for 1900, p. 443, and this Journal, 24, 140.

Between the conglutin from the blue lupine and the less soluble no difference in the proportion of nitrogen belonging to the different groups. The more soluble globulin of the yellow lupine, different groups. The more soluble globulin of the yellow lupine, which contains a much larger proportion of sulphur, yields a distinctly greater amount of ammonia than do the other preparations, as shown by the figures given last in the table. Whether or not this excess of ammonia, as well as that of the sulphur, is caused by some non-protein substance combined with the conglutin of these fractions is not shown by these determinations.

### *Corylin.*

In the hazel nut, *Corylus*, and English walnut, *Juglans regia*, is a large quantity of globulin to which the writer gave the name corylin.<sup>1</sup> We have recently obtained from the American black walnut a similar globulin which closely resembles that contained in the two nuts first mentioned. The proportion of nitrogen in the different groups in these globulins was found to be as follows:

#### PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN CORYLIN.

Source.			Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Hazel nut ( <i>Corylus</i> ) .....	I	a	2.17	5.56	....	...	19.02
	II	b	2.22	5.94	10.70	0.16	....
Black walnut ( <i>Juglans nigra</i> ) .....	I	a	1.85	5.21	11.68	0.10	18.90
	II	b	1.71	5.61	11.33	0.19	....

The distinctly smaller proportion of ammonia nitrogen obtained from the black walnut globulin indicates a difference between these two proteins. The fact that these seeds are not closely related botanically, likewise makes this more probable and renders necessary a strict comparison of these two proteins with that of the English walnut, which will be made as soon as a supply of the globulin from the latter nut is obtained.

### *Other Plant Globulins.*

The following table gives the results of our determinations of the proportion of the different forms in which the nitrogen was found in proteins which we have thus far obtained from the seeds of but one species of plants.

<sup>1</sup> Report Conn. Agr. Exp. Sta. for 1895, p. 268, and this Journal, 18, 609 (1896).

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN VARIOUS  
PLANT GLOBULINS.

Protein.	Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Excelsin—Brazil nut ( <i>Bertholletia excelsa</i> ).....		{ a	1.45	...	....	...	....
		{ b	1.50	5.76	10.97	0.17	18.30
Amandin—Almond ( <i>Prunus Amygdalus</i> var <i>dulcis</i> ) .....		{ a	3.03	4.09	....	...	19.00
		{ b	3.06	4.21	11.55	0.18	....
Vignin—Cowpea ( <i>Vigna catjang</i> ) ..		{ a	1.91	4.28	10.81	0.25	17.25
		{ b	1.91	...	....	...	....
Glycinin—Soy bean ( <i>Glycine hispida</i> ) .....		{ a	2.11	4.00	11.26	0.08	17.45
		{ b	2.12	3.90	11.27	0.16	....
Avenalin—Oat ( <i>Avena sativa</i> ) .....		b	2.37	3.94	11.37	0.22	17.90

Amandin yields a larger proportion of nitrogen as ammonia than any of the other globulins and about the same proportion of basic nitrogen as the average of the majority of the other proteins examined. In this respect it differs from the other globulins rich in nitrogen which yield a much larger amount of basic nitrogen. Amandin must, therefore, have a decidedly different structure from these. The figures given in this table for the other proteins require no special comment.

NITROGEN IN THE DIFFERENT GROUPS IN ALCOHOL-SOLUBLE  
PROTEINS.

Kossel and Kutscher<sup>1</sup> have recently decomposed the alcohol-soluble proteins of wheat and maize kernels and have determined the proportion of ammonia, histidine and arginine which results. They found that lysin was entirely absent, although this diamino acid had been found in all the proteins previously examined, and also that the proportion of arginin was much less than that found in other proteins.

The results of our determinations by Hausmann's method of the different forms of nitrogen in several alcohol-soluble proteins are in harmony with the results obtained by Kossel and Kutscher, as the following table shows:

<sup>1</sup> *Ztschr. physiol. Chem.*, 31, 165.

## PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN ALCOHOL-SOLUBLE PROTEINS.

Protein.	Source.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Gliadin—Wheat ( <i>Triticum vulgare</i> )		<i>a</i>	4.20	1.18	....	...	17.66
		<i>b</i>	4.34	1.00	12.25	0.07	....
		<i>b</i>	4.36	...	....	0.20	....
Gliadin—Rye ( <i>Secale cereale</i> ) .....		<i>a</i>	3.94	0.95	....	...	17.72
		<i>b</i>	4.15	0.87	12.59	0.11	....
		<i>b</i>	4.22	0.92	12.39	0.20	....
Hordein—Barley ( <i>Hordeum vulgare</i> )		<i>a</i>	3.96	0.66	....	...	17.21
		<i>b</i>	4.06	0.88	12.04	0.23	....
		<i>a</i>	2.95	0.67	12.46	0.05	16.13
Zein—Maize ( <i>Zea mays</i> ) ....		<i>b</i>	3.00	0.40	12.49	0.24	....
		<i>b</i>	2.98	0.48	12.45	0.22	....
		<i>b</i>	3.01	...	....	...	....
		<i>b</i>	2.93	0.40	12.68	0.12	....
		<i>b</i>	2.98	...	....	...	....
Alcohol-soluble protein—Oat ( <i>Avena sativa</i> ).....	I	<i>b</i>	3.55	1.04	10.85	0.26	15.70
		<i>b</i>	3.67	1.07	10.68	0.28	....
	II	<i>b</i>	3.37	1.46	10.59	0.23	15.65
		<i>b</i>	3.50	1.38	10.56	0.21	....
Bynin—Malt ( <i>Hordeum vulgare</i> )...	I		3.79	0.80	11.11	0.56	16.26
	II		3.86	0.70	11.23	0.47	....

Kossel and Kutscher<sup>1</sup> made determinations of the diamino acids in preparations believed to represent the three alcohol-soluble proteins, mucedin, gliadin and gluten fibrin, which Ritt-hausen<sup>2</sup> described as constituents of wheat gluten, and state that their preparations were made according to Ritt-hausen's directions. Unfortunately, the writer has never been able to understand Ritt-hausen's explanation of the process by which these three proteins were prepared, although he has devoted much time and attention to its description. We have been unable, therefore, to prepare products which could be considered to fairly represent these three proteins, but the very extensive study of a large number of fractions obtained from alcoholic solutions of every possible strength failed to give Osborne and Voorhees<sup>3</sup> any evidence whatever of the existence in the wheat kernel of more than one protein which

<sup>1</sup> *Ztschr. physiol. Chem.*, 31, 165.

<sup>2</sup> "Die Eiweisskörper, etc.," Bonn, 1872.

<sup>3</sup> *Am. Chem. J.*, 18, 392.

is soluble in alcohol. Kjeldahl<sup>1</sup> came to the same conclusion, as he says there can be only one alcohol-soluble protein in wheat since both composition and  $[\alpha]_D$  are constant.

The only noticeable difference which Kossel and Kutscher found between their preparations of so-called gluten fibrin, gliadin and mucedin lay in the proportion of histidine. The amount of this substance found in their gliadin was a little less than in gluten fibrin and distinctly less in their mucedin than in the other two preparations. As only one determination was made in each of these products, the figures given require confirmation before the differences, which, as Kossel and Kutscher say, "are at the most only very slight," can be accepted as evidence of the presence of three alcohol-soluble proteins in the wheat kernel.

The nitrogen belonging to the histidine and arginine, which Kossel and Kutscher found, formed 1.39 per cent. of the gluten fibrin, 1.13 per cent. of the mucedin and 1.21 per cent. of the gliadin, which is equal to a mean of 1.24 per cent. in the three preparations. The amount of nitrogen which we precipitated by phosphotungstic acid from the solution of the decomposition products of gliadin falls a little below this figure, as would be expected from the known solubility of arginine phosphotungstate, of which this precipitate chiefly consisted. Gulewitsch<sup>1</sup> found when arginine is precipitated from 100 cc. of solution by phosphotungstic acid that 7 milligrams remain dissolved. This amount of arginine contains 2.2 milligrams of nitrogen which, if added to the average quantity found by us to be precipitated by phosphotungstic acid, gives 1.2 per cent. of basic nitrogen against 1.24 per cent. found by Kossel and Kutscher.

The amount of nitrogen in the arginine and histidine which Kossel and Kutscher found in zein was equal to 0.8 per cent. of the protein. If the amount of nitrogen corresponding to the solubility of arginine phosphotungstate is added to the average of our determinations of the basic nitrogen in zein, we have 0.71 per cent., which agrees very closely with Kossel and Kutscher's result.

The amount of nitrogen as ammonia which Kossel and Kutscher obtained from these alcohol-soluble proteins was decidedly less than that found by us, doubtless because a part of the ammonia was precipitated from their solutions with the humus substance.

<sup>1</sup> *Agriculturchem. Centrbl.*, 28, 197 (1892).

<sup>2</sup> *Ztschr. physiol. Chem.*, 27, 196.



These investigators also determined the proportion of diamino acids in the protein of wheat gluten that is insoluble in alcohol which they, following Ritthausen, call gluten casein, but which we prefer to call glutenin, since no near relation between it and the milk caseins exists, as was formerly supposed. The results of our determinations of the different groups of nitrogen in this protein were the following:

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN GLUTENIN.

Source.	Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Wheat gluten.. { $\delta$	3.26	1.90	12.18	0.15	17.49
{ $\delta$	3.35	2.20	11.71	0.23	....

Kossel and Kutscher found in glutenin 2.14 per cent. of nitrogen belonging to the diamino acids, histidine, arginine and lysine, with which figure the average of ours of 2.05, or, allowing for the solubility of arginine phosphotungstate, 2.27 is in good agreement. The amount of ammonia which they found was, as for the other proteins examined, less than that which we found, namely, 2.02 per cent. as against 3.31 per cent. found by us.

Kossel and Kutscher think that it is probable that, under the condition of their experiments, some of the ammonia unites with the humus, as suggested by Udransky,<sup>1</sup> and is estimated with the nitrogen of that substance.

Hart<sup>2</sup> has since found that on adding sodium chloride or sodium sulphate to the sulphuric acid with which he decomposed the proteins, that the amount of ammonia nitrogen was increased and that of the humus correspondingly diminished, which shows that a part of the ammonia is removed when the humus is separated from the solution before distilling with magnesia. By decomposing zein under these conditions, Hart found 2.65 per cent. of nitrogen as ammonia and none in the humus precipitate. That he found less than we is probably because he used barium carbonate instead of magnesia to expel the ammonia, though he does not say definitely that he did so. He has shown that barium carbonate yields less ammonia than

<sup>1</sup> *Zschr. physiol. Chem.*, 12, 42.

<sup>2</sup> *Ibid.*, 33, 347.

magnesia, as the latter, according to his view, acts on some of the nitrogenous substances other than ammonium salts.

In conclusion we give some results, obtained with very pure preparations of casein, crystallized ovalbumin, conalbumin and nucleovitellin from the yolk of hen's eggs.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN SOME ANIMAL PROTEINS.

Protein.		Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Casein .....	{a	1.65	3.46	....	...	15.62
	{b	1.58	3.53	10.30	0.21	....
Ovalbumin ...	{a	1.35	3.22	....	...	15.51
	{b	1.32	3.38	10.52	0.29	....
Conalbumin ...	{b	1.23	4.10	10.57	0.21	16.11
	{b	1.18	4.21	10.41	0.31	....
Nucleovitellin .	{b	1.21	4.60	10.28	0.9	16.28
	{b	1.28	4.69	10.07	0.24	....

The conalbumin was obtained by removing from an ammonium sulphate solution of egg white all of the crystallizable ovalbumin and then separating the protein substance which was deposited in spheroids by further evaporation. The aqueous solution of the latter substance was dialyzed in distilled water until all the ammonium sulphate was removed and the conalbumin coagulated by heating to 60°. The composition and properties of conalbumin are given in a recent paper by Osborne and Campbell,<sup>1</sup> whose observations respecting conalbumin have since been confirmed by Langstein.<sup>2</sup>

As conalbumin closely resembles ovalbumin in properties and composition, it seemed quite possible that it consisted simply of a compound of the latter with some other substance and that the protein part of the molecules of the two albumins might be the same. The results of our determinations show such wide differences in the proportion of basic nitrogen that there can be little doubt that these albumins are two distinctly different substances. Schulze<sup>3</sup> has come to the same conclusion as a result of his study of the "gold numbers" of these two albumins.

<sup>1</sup> Report Conn. Agr. Expt. Sta. for 1899, p. 348; also this Journal, 22, 422.

<sup>2</sup> Hofmeister's "Beiträge," 3, p. 83 (1901).

<sup>3</sup> *Ibid.*, 3, p. 137 (1902).

The amount of nitrogen as ammonia which we obtained from crystallized ovalbumin, namely, 1.35 per cent., is in very close agreement with the 1.32 per cent. found by Hausmann. Likewise we both found nearly the same amount of basic nitrogen, 3.22 and 3.31 per cent., whereas Kossel and Kutscher found considerably more, *i. e.*, 4.19. We have, unfortunately, been unable to find the conditions under which this last figure was obtained, it being quoted by Kutscher without reference to any publication. As the ovalbumin used does not appear to have been crystallized ovalbumin, it is possible that conalbumin may have contributed to the higher result.

Our determinations of nitrogen as ammonia yielded by milk casein agree with those calculated from Kutscher's figures, assuming that his casein contained 15.62 per cent. of nitrogen. Kutscher thus found 1.62, 1.62, 1.58 and 1.59 per cent. of nitrogen in this form. Hart<sup>1</sup> found 1.60 per cent. by distilling the decomposition products of casein with magnesia and 1.39 and 1.18 per cent. by distilling with barium carbonate the decomposition products obtained by boiling with sulphuric acid without adding sodium chloride and 1.52 per cent. after adding this salt.

Hart found that more lysine was obtained from the decomposition products of casein when the latter was boiled with sulphuric acid and sodium chloride than when boiled with sulphuric acid alone. He found, when using sulphuric acid and salt, an amount of histidine, arginine and lysine corresponding to 3.37 per cent. of basic nitrogen in the casein, which agrees closely with our result by Hausmann's method, namely, 3.49 per cent.

Gümbel<sup>2</sup> found, by Hausmann's method, nitrogen as ammonia corresponding to 1.62 per cent. of milk-casein and to 4.23 per cent. of basic nitrogen, the former being in close agreement with our results, but the latter considerably higher than those found by us or by Hart, who determined the bases directly.

If the results of the determinations by Hausmann's method, as employed by us, are compared with the results obtained by Kossel and Kutscher's method, in separating and determining the actual quantity of the diamino acids produced by decomposing comparatively large quantities of the protein substances, it will be seen that nearly the same amounts of basic nitrogen are obtained by both methods. In the following table we give the figures obtained by

<sup>1</sup> *Ztschr. Physiol. Chem.*, 33, 347 (1901).

<sup>2</sup> Quoted by Hofmeister, "*Ergebnisse der Physiol.*," Vol. I, p. 777.

the two methods, the amount of nitrogen found by Hausmann's method being increased by the addition of a quantity of nitrogen corresponding to the solubility of arginine phosphotungstate.

PERCENTAGE OF BASIC NITROGEN IN SEVERAL PROTEINS.

Zein .....	{ 0.80 by Kossel and Kutscher's method. 0.71 by Hausmann's modified method.
Gliadin...	{ 1.24 by Kossel and Kutscher's method. 1.20 by Hausmann's modified method.
Glutenin .	{ 2.14 by Kossel and Kutscher's method. 2.27 by Hausmann's modified method.
Casein ...	{ 3.37 by Kossel and Kutscher's method. 3.71 by Hausmann's modified method.

These results indicate that Hausmann's method, as we have applied it, gives a fairly accurate measure of the true proportion of nitrogen belonging to the diamino acids. Before this can be demonstrated, however, quantitative determinations by Kossel and Kutscher's method must be made in other proteins, especially those yielding larger proportions of diamino acids.

An examination of the figures showing the different forms of binding of the nitrogen in the many proteins which we have investigated shows that these vary chiefly in the proportion of ammonia and basic nitrogen which they yield. In the following table we give the average of the figures found for each of these proteins, arranged in the order of amount of basic nitrogen.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN VARIOUS PROTEIN BODIES.

Protein.	Source.	Nitrogen as ammonia.	Basic nitrogen.	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Globulin—Wheat .....		1.42	6.83	9.82	0.28	18.39
"	Cocoanut . . . . .	1.36	6.06	10.92	0.14	18.48
"	Squash seed .....	1.28	5.97	11.04	0.22	18.51
Edestin—Hemp seed .....		1.88	5.91	10.78	0.12	18.64
Excelsin—Brazil nut .....		1.48	5.76	10.97	0.17	18.30
Corylin—Hazel nut .....		2.20	5.75	10.70	0.16	19.00
Globulin—Cotton seed .....		1.92	5.71	11.01	...	18.64
"	Castor bean .....	1.96	5.64	11.00	0.12	18.75
Corylin—Walnut .....		1.78	5.41	11.51	0.15	18.84
Conglutin—Lupine .....		{ a 2.12	5.20	10.38	0.18	17.90
		{ b 2.65	5.13	10.30	0.14	18.21

Protein.	Source.	Nitrogen as ammonia.	Basic nitrogen	Non-basic nitrogen.	Nitrogen in magnesium oxide precipitate.	Total nitrogen.
Legumin—	Pea, lentil, horse bean, vetch.....	1.69	5.18	10.92	0.17	17.97
Globulin—	Flax seed.....	2.00	4.77	11.47	0.22	18.48
Vicilin—	Pea, lentil, horse bean ...	1.78	4.75	10.37	0.21	17.11
Nucleovitellin—	Egg yolk.....	1.25	4.65	10.16	0.22	16.28
Vignin—	Cow pea.....	1.91	4.28	10.81	0.25	17.25
Globulin—	Sunflower.....	2.57	4.27	11.52	0.24	18.58
Conalbumin—	Egg white.....	1.21	4.16	10.49	0.26	16.11
Amandin—	Almond.....	3.05	4.15	11.55	0.17	19.00
Phaseolin—	Kidney bean, adzuki bean.....	1.74	3.97	10.18	0.29	16.20
Glycinin—	Soy bean.....	2.11	3.95	11.27	0.12	17.45
Legumelin—	Pea, lentil, horse bean, adzuki bean.....	1.04	3.71	10.96	0.38	16.09
Leucosin—	Wheat.....	1.16	3.50	11.83	0.43	16.93
Casein—	Cow's milk.....	1.61	3.49	10.31	0.21	15.62
Ovalbumin—	Egg white.....	1.34	3.30	10.58	0.29	15.51
Glutenin—	Wheat gluten.....	3.30	2.05	11.95	0.19	17.49
Gladin—	Wheat, rye.....	4.20	0.98	12.41	0.14	17.66
Hordein—	Barley.....	4.01	0.77	12.04	0.23	17.21
Zein—	Maize.....	2.97	0.49	12.51	0.16	16.13

The most striking feature shown by this table is the wide range in the amounts of basic nitrogen obtained from the different proteins. While the difference between the highest total nitrogen and the lowest is 3.49 per cent. of the protein, or 18.3 per cent. of the highest nitrogen, that between the highest basic nitrogen and the lowest is 6.34 per cent., a difference of 92.7 per cent. of the highest figure. The proportion of ammonia yielded by these different proteins likewise differs greatly, the difference between the highest and lowest figures being 3.16 per cent. or 75.2 per cent. of the highest figure. The non-basic nitrogen, on the other hand, is much more constant even than the total nitrogen, the difference between the highest and lowest being only 2.69 per cent. of the protein or 21.5 per cent. of the highest figure.

Apart from the alcohol-soluble proteins, which all come together at the end of the table, no other relation depending on the proportion of basic nitrogen is apparent.

The crystalline globulins from the hemp seed, squash seed and flax seed, as we have already said, are so nearly alike in solubility, reactions, crystalline form and composition that a most rigid comparison has as yet failed to reveal any differences which indicated that they are not one and the same chemical individual; nevertheless the globulin from the flax seed differs from the other two in the amount of basic nitrogen which it yields by over 1 per cent. and the globulin from the squash seed differs in the amount of ammonia which it yields by about 0.6 per cent. The molecules of these globulins evidently have a different structure.

In the table, all of the proteins down to legumelin are globulins, with the exception of the nucleovitellin, which, however, as obtained originally from the egg yolk in combination with lecithin, has the properties characteristic of globulin, but after washing with alcohol it passes into the condition in which it was used for these experiments, in which it is no longer soluble in saline solutions. Legumelin and ovalbumin, the proteins next following in the table, are soluble in water and in this respect differ from those preceding them, but no difference in the proportion of basic nitrogen exists between legumelin and phaseolin, which is a pronounced globulin, and ovalbumin does not contain very much less.

Those proteins which are characterized by dissolving in strong alcohol present, on the other hand, a marked contrast to the others, in that they all yield far less basic nitrogen and more ammonia than the others, with the single exception of amandin which yields the same amount of ammonia as does zein but over eight times as much basic nitrogen.

The larger proportion of nitrogen which characterizes so many of the proteins of seeds, compared with the nitrogen in animal proteins, appears to be caused by a larger proportion of substances yielding ammonia and basic products. Some of the plant globulins contain nearly as much basic nitrogen as corresponds to the nitrogen content of the histidine, arginine and lysine which Kossel and Kutscher found in the histone from the thymus gland, namely, 6.43 per cent., while the globulin of wheat contains even more. If, as seems probable, the basic nitrogen of these vegetable proteins shall be shown by further investigation to belong wholly to the three diamino acids named, it would appear that the basic properties of the proteins are not caused simply by the diamino acid

components of their molecules, as Kossel and Kutscher suggest, for the histones are much stronger bases than any of these vegetable proteins.

This wide variation in the proportion of basic decomposition products of the various proteins, as Kossel and Kutscher point out, raises important questions regarding their food value.

At Kossel's suggestion, Szumoski,<sup>1</sup> after feeding geese and doves with maize for long periods, examined their various organs and tissues for zein, with negative results. That, however, zein is, in fact, assimilated is, in Szumoski's opinion, proved by the experiments which Grandeau, Leclerc and Ballacey<sup>2</sup> made with horses, and Rubner<sup>3</sup> made with men.

Feeding experiments with "gluten meal" present much stronger evidence on this point, since they show that the proteins of this meal are quite as well assimilated as those of cotton seed meal.

The "gluten meal" used in these experiments is a product of the manufacture of maize starch and contains a large proportion of the alcohol-soluble zein. The proportion of alcohol-soluble zein has not been accurately determined and doubtless varies with the different samples, but in a large number examined at different times by the writer not far from 25 per cent. of these meals were found to consist of alcohol-soluble zein.

The digestibility of the proteins of gluten meal has been found, as the average of several experiments, to be 88.2 per cent., while that of cotton seed meal is 88.4 per cent.,<sup>4</sup> from which it is evident that the proteins of gluten meal possess a high coefficient of digestibility, and as these consist largely of zein, it is almost certain that zein is assimilated without special difficulty.

In order to show the relative proportions of the several groups of nitrogenous decomposition products yielded by these meals when treated with boiling acids, we took a portion of each meal containing 0.1600 gram of nitrogen, and treated it in exactly the same way as described in this paper for the proteins. The results were as follows:

<sup>1</sup> *Ztschr. physiol. Chem.*, 26, 198.

<sup>2</sup> *Ann. de la Science Agronomique*, 9, Ann., T. I., 1892.

<sup>3</sup> *Ztschr. Biol.*, 15, 150 (1879).

<sup>4</sup> Bulletin 77, Office of Experiment Stations, U. S. Dept. of Agr.

PERCENTAGE OF NITROGEN IN THE DIFFERENT GROUPS IN THE PROTEINS  
OF THE MEAL, ASSUMING THESE TO CONTAIN 16 PER CENT.  
OF NITROGEN.

	Cotton seed meal.	Gluten meal.
Nitrogen as ammonia.....	1.52	2.38
Basic nitrogen.....	4.97	1.42
Non-basic nitrogen .....	8.67	11.63
Nitrogen in magnesium oxide precipitate ..	0.84	0.57
Total nitrogen .....	16.00	16.00

These figures show how great the difference is between the proportions of these several nitrogenous groups and, since no apparent difference in food value exists between these meals, it would seem as if, from the standpoint of nutrition, these very decided chemical differences were of but little importance.

Since zein contains 16 per cent. of nitrogen, the figures given for the gluten meal may be directly compared with those of zein. As the globulin of the cotton seed contains 18.6 per cent. of nitrogen, the amount of meal taken corresponded to only 0.8608 gram. If we calculate the figures given for cotton seed meal to this basis, they become comparable with those of the cotton seed globulin. In the following table the results of this comparison are shown.

	Protein in cotton seed meal.	Globulin of cotton seed meal.	Zein.	Protein in gluten meal.
Nitrogen as ammonia ..	1.77	1.92	2.97	2.38
Basic nitrogen .....	5.77	5.71	0.49	1.42
Non-basic nitrogen.....	10.12	11.01	12.51	11.63
Nitrogen in magnesium oxide precipitate...	0.98	....	0.16	0.57
Total nitrogen .....	18.64	18.64	16.13	16.00

From these figures it appears that the total protein of the cotton seed meal yields practically the same proportion of decomposition products as the cotton-seed globulin, the differences shown being unquestionably due to the greater amount of humus arising from the carbohydrates, whereby a larger amount of nitrogen appears in the "MgO pp." and a smaller amount as ammonia. In the case of gluten meal, it is evident that some protein other than zein is also present, but its proportion is not indicated by the figures. Loewi<sup>1</sup> has just shown that a dog can be kept in nitrogenous

<sup>1</sup> *Archiv. f. Exper. Path. u. Pharm.*, 48, 303 (1903).



equilibrium or even gain nitrogen when fed with food containing protein decomposition products which are wholly free from any substance giving the biuret reaction, that is, with food containing no protein whatever. The animal can therefore synthesize protein from a mixture of the crystallizable products produced by decomposition of protein. Since such a wide difference exists between the proportions in which the several groups of products are yielded by the different food proteins, this synthesis must consist in something more than a recombination of the several fractions of the molecule of the food protein; it must involve a more or less extensive alteration of these fractions and conversion of one into another before the requisite number of groups of proper nature are at hand from which the new molecule can be constructed.

If we consider the probable number of these groups and the many kinds of them which must take part in this synthesis, the selective and constructive power of the cells in which this process takes place appears to be very great. Hofmeister<sup>1</sup> states that if a mean molecular weight of 130-140 is assumed for the splitting products of the protein molecule, there must be at least 40 such groups in the protein molecule if its molecular weight is 5,000, or 120 groups if it is 15,000.

There are already about twelve different kinds of these groups known which are primary decomposition products of the protein molecule. The complexity of the process whereby the new protein molecule is constructed from the decomposition products of the food protein is thus easily apparent.

The fact that so many of the vegetable proteins, which serve extensively as food, have been shown, by our present investigation, to yield such different proportions of the various nitrogenous decomposition products, as compared with the animal proteins, makes it a matter of the greatest interest and importance to know something more of the processes involved in this synthesis.

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<sup>1</sup> "Ergebnisse der Physiol.," Vol. I, p. 774.

[CONTRIBUTION FROM THE BIOCHEMIC LABORATORY B. A. I. AGR. DEPT.,  
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## THE COMPOSITION OF THE TUBERCLE BACILLI DERIVED FROM VARIOUS ANIMALS.<sup>1</sup>

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CONTINUING our work as published in this Journal, 17, 605; 18, 449; 20, 618, we have submitted to examination tubercle bacilli from various sources; namely, bovine bacilli, swine bacilli, horse bacilli, avian bacilli, attenuated human bacilli and virulent human bacilli.

In preparing these germs for analyses all were grown upon liquid media. After the cultures had been allowed to develop for a sufficient length of time, they were all filtered in the same way, washed in the same way so as to remove from the germs themselves, any mechanically adherent culture media, and necessarily at the same time, a large portion of the water-soluble matter. The germs, subsequently dried *in vacuo*, were submitted to analysis, first by extracting with ether, then with alcohol and then with chloroform. A comparison of the amounts of these extracts shows that the largest percentage of fat was obtained from the attenuated human bacilli, and from the others in the following order: Horse, virulent human, bovine, avian, swine.

In our earlier article upon the mineral constituents of the tubercle bacilli, published in this Journal, 18, 449, the percentage of phosphoric pentoxide was found to be a little over 55 in the human germ. As will be noted in Table II, the percentage of phosphoric pentoxide in these human germs was found to be, in the virulent, over 60 per cent., in the attenuated over 70 per cent. In comparing these figures with the earlier results, it should be remembered that the germs used for obtaining the earlier data were grown upon the ordinary glycerine media to which no phosphates had been added, while all of the present germs were grown upon a medium intentionally rich in phosphates. The amount of material available for the phosphoric pentoxide determinations here reported was also small, so that there may be some slight error due to manipulation, but allowing for these facts, it is very evident that all of these tubercle bacilli

<sup>1</sup> Read at the Washington meeting of the American Chemical Society.

are voracious consumers of phosphoric oxide, in which property they correspond to a great many other plants.

Aronson's assumption that the extractive matter of the tubercle bacilli was very largely fatty acids, a conclusion which does not follow from the methods that he has reported in his article, led us to make some preliminary determinations of the possible free acid present in our various extracts. Kresling concluded that the chloroform extract of the human tubercle bacilli contains about 14 per cent. of free fatty acid. Our determinations of the possible free fatty acid were based upon the acid value as secured by titration with N/10 sodium hydroxide. The results are recorded in Table III.

The acid value was determined both in the ether and alcohol extracts separately. The total acid value noted in Table III shows that the highest acid value was obtained from the virulent human and the others in the following order: Swine, attenuated human, avian, bovine and horse. In the last column are given the total percentages of the free acids in the whole germ counted as oleic acid. The acids were all calculated as oleic for the purpose of making a satisfactory basis for comparison.

Until we have completed the determinations of the exact character of the ether, alcohol and chloroform extracts obtained from these various bacilli, which are in progress at present, much speculation in regard to the relation of the composition of the germ to its character and virulence is not warranted. It is interesting to note, however, that the percentage of alcohol extract obtained from the avian bacilli is very much greater than that obtained from any of the other germs, while the percentage of chloroform extract in the bovine bacilli and virulent human bacilli is almost exactly the same, there being but little chloroform extract obtained from the horse, swine and avian germs, while a considerably larger amount is secured from the attenuated human germ. The variation in the amount of ether extract has already been noted. The results certainly indicate that as there is a variation in the morphology of tubercle bacilli derived from different sources, depending upon their surroundings, so there is a variation in the composition of the germ cells themselves. They show, further, a point which should be especially emphasized, that there is a greater difference between the two human germs, the

one attenuated, non-pathogenic for guinea pigs, the other almost as pathogenic for guinea pigs as the bovine germ, than there is between the virulent human and the bovine and horse bacilli. It is certainly not an unwarranted assumption that possibly this loss of virulence in the human germ is due to the fact that the bacilli have acquired through their prolonged saprophytic existence, and their consequent immunity from the attacks of phagocytes and other protective substances of the animal body, the property of producing smaller amounts of poisonous substances, while in the case of the virulent human bacilli, the bovine, horse and swine germs, which do not produce nearly so large an amount of harmless fatty substances, and consequently contain a lower percentage of extractive matter, the relative amount of poisonous proteid produced is greater. That this proteid matter, belonging to the class of nucleoproteids, as was already pointed out by ourselves in 1895 in the article above referred to, is one of the principal poisons of the tubercle bacilli, has been well demonstrated; and if the bacilli are able to produce larger amounts of these poisonous substances, it would necessarily follow that they are much more virulent. A further study of these proteid substances is in progress, as well as the identification of the free fatty acids, fats, waxes and other extractive material.

As pointed out by the writers in 1897,<sup>1</sup> there is present in the cultures of human bacilli a very virulent acid-like necrotic substance readily soluble in water. This substance, as well as those of a similar nature, was necessarily extracted in the preparation of the germs for analysis, and hence does not come into consideration in this report.

Our results here recorded indicate the relationship between the tubercle bacilli derived from various sources and emphasize the difference between attenuated and virulent human tubercle bacilli. It must be remembered that these analyses were only upon one representative of each of the different bacilli, yet the results in the human germs correspond so closely with those obtained in 1895 and also those reported by other workers, that we can assume a like composition for the bacilli obtained from similar sources.

<sup>1</sup> De Schweinitz and Dorset : *Centrbl. f. Bakt. u. Parasit.*, Abt. 1, 22, 209 (1897).

TABLE I.—ETHER, ALCOHOL AND CHLOROFORM EXTRACTS OF TUBERCLE BACILLI.

	Bovine bacilli.		Swine bacilli.		Horse bacilli.	
	1.	2.	1.	2.	1.	2.
	Per cent.	Average.	Per cent.	Average.	Per cent.	Average.
Ether extract.....	17.74	17.66	13.69	11.43	22.90	23.87
Alcohol extract.....	.....	8.13	.....	7.83	8.18	8.18
Chloroform extract.....	.....	0.49	.....	0.20	0.29	0.12
Total extracts.....	.....	26.32	.....	19.46	31.37	31.76
	Avian bacilli.		Attenuated human bacilli.		Virulent human bacilli.	
	1.	2.	1.	2.	1.	2.
	Per cent.	Average.	Per cent.	Average.	Per cent.	Average.
Ether extract.....	17.40	17.32	28.86	28.59	20.40	20.22
Alcohol extract.....	13.15	13.39	7.22	7.49	7.21	7.23
Chloroform extract.....	0.04	.....	1.33	(1.33)	0.48	(0.48)
Total extracts.....	30.59	30.71	37.41	37.41	28.09	27.93

TABLE III.—ACID VALUE OF ETHER AND ALCOHOL EXTRACTS OF TUBERCLE BACILLI.

	Acid value.		Total acid value, calculated on the sum of ether and alcohol extract.		Free acids in alcohol and ether extracts.		Free acids calculated for whole substances.		Total free acids in bacilli.	
	Ether extract.	Alcohol extract.	Ether extract.	Alcohol extract.	Ether extract.	Alcohol extract.	Ether extract.	Alcohol extract.	Ether extract.	Alcohol extract.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Bovine bacilli.....	9.43	20.40	12.90	13.97	4.74	10.25	0.83	0.83	1.66	1.66
Swine bacilli.....	8.02	23.45	13.97	11.46	4.03	11.78	0.46	0.92	1.38	1.38
Horse bacilli.....	9.36	18.47	11.46	13.04	4.70	9.28	1.09	0.75	1.84	1.84
Avian bacilli.....	13.00	13.11	13.04	13.13	6.53	6.59	1.13	0.87	2.00	2.00
Human bacilli (atten.).....	12.77	14.57	13.13	14.63	6.41	7.32	1.84	0.53	2.37	2.37
Human bacilli (vir.).....	14.02	16.45	14.63	.....	7.04	8.26	1.42	0.59	2.01	2.01

TABLE II.—ASH AND PHOSPHORUS IN TUBERCLE BACILLI.<sup>1</sup>

	Moisture. Per cent.	Ash. Per cent.	P <sub>2</sub> O <sub>5</sub> in dry bacilli. Per cent.	P <sub>2</sub> O <sub>5</sub> in ash. Per cent.
Bovine bacilli.....	{ 2.42 2.48	2.66 2.67	1.56 1.55	58.54 58.04
Swine bacilli.....	{ 2.26 2.06	2.37 2.31	1.30 1.31	55.00 56.48
Horse bacilli.....	{ 2.27 2.42	3.63 3.55	2.07 2.02	55.68 55.40
Avian bacilli.....	{ 2.40 ....	3.96 3.94	2.22 2.19	55.98 55.63
Human bacilli (atten.)....	{ 2.67 2.58	2.44 2.31	1.79 1.71	73.49 74.38
Human bacilli (vir.).....	{ 3.91 3.70	3.94 3.92	2.50 2.38	63.47 60.90

<sup>1</sup> Determinations by James A. Emery.

[CONTRIBUTION FROM THE LABORATORY OF THE BUREAU OF INTERNAL REVENUE, U. S. TREASURY DEPARTMENT.]

THE COMPOSITION OF PROCESS OR RENOVATED BUTTER.<sup>1</sup>

BY CHARLES A. CRAMPTON.

Received January 3, 1903.

THE Act of May 9, 1902, makes this product, as specifically defined therein, subject to Federal control, placing its production, transportation and sale under restrictions similar to those imposed upon oleomargarine, which product is also made the subject of new legislation by the same act.

Without entering into detail concerning the provisions of the new law, its main features may be briefly stated, as follows: It defines two classes of oleomargarine, one taxable at  $\frac{1}{4}$  cent per pound, and the other at 10 cents per pound, and three classes of butter. Of the latter, one class is normal or statutory butter, defined for purposes of comparison, and exempt, of course, from taxation or supervision; one class is "process or renovated butter," taxable at  $\frac{1}{4}$  cent per pound, the same rate as that laid upon oleomargarine free from artificial coloration; and the third class is "adulterated butter," subject to a tax of 10 cents per pound, the same rate as artificially colored oleomargarine.

The sale of renovated butter is not so closely regulated as that of oleomargarine, as no special tax is required from wholesale or retail dealers, so that government control does not follow it to the

<sup>1</sup> Read at the Washington meeting of the American Chemical Society.

purchaser. The clause concerning the prohibition of ingredients deleterious to health in oleomargarine is not made applicable to renovated butter, but the manufacture of the latter product is made subject to the supervision of the Bureau of Animal Industry of the Department of Agriculture, a provision doubtless intended to serve the same purpose. Moreover, by a somewhat peculiar interweaving of definitions, renovated butter loses its status as such, and becomes "adulterated butter" under certain conditions, and is then subject to the high rate of tax imposed upon that product. During the first three months of the operation of the law, there were produced in the United States, as shown by the Annual Report of the Commissioner of Internal Revenue for 1902, 5,879,833 pounds of renovated butter, about one-half as much as the total quantity of oleomargarine produced during the same period.

Subject to the control of two different departments of the general government, and also to restrictive laws in many of the States, renovated butter has come to be a product of considerable interest to chemists, and it is highly desirable to obtain some knowledge of the character of the changes undergone by the butter-fat in the processes to which it is subjected by the methods employed. A brief description of the ordinary methods of renovation as practiced in most of the factories at the present time may not be amiss. The raw material or "stock," as it is termed, consists of butter which is not salable for direct consumption, either because it has deteriorated through rancidity, mold, or other causes, or because it was produced by careless or ignorant makers, who were unable to give it an attractive appearance or flavor. The country grocery store, which assembles small lots or parcels of butter from many makers, and dumps all together, indiscriminately, good, bad, and indifferent, is the recruiting ground for most of the material. In the earlier days of the industry, the stock obtainable for renovating purposes was but a shade better than the soap-fat grade, but competition has advanced the price, and the increased demand has secured a more prompt marketing of the material, so that much of it has not greatly deteriorated from its original condition when it reaches the renovating factory. The character of the renovated product has correspondingly improved, especially in its keeping qualities. The best grades approximate the lower grades of creamery butter, the chief defect

being the loss of "grain" through the operation of melting, a quality which is only partially restored by subsequent granulation in ice water.

The first step in the process is the separation of the fat from the water and curd by melting and settling. The curd and salt water are drawn off from beneath the oil, or sometimes the whole is passed through a separator. Whatever bad flavor is inherent in the curd is separated in this operation, and the fat is ready for the next treatment, which is the aeration or "blowing" with air. This is sometimes supplemented by a bath of water, and renovators have been accused of using chemical agents at this stage of the procedure, but they claim that such treatment has not been found successful, doubtless from the tendency towards saponification, and that the main reliance is upon the blowing to remove disagreeable odors, and leave a fairly neutral fat. This is then emulsified with fresh milk, which has been inoculated with a bacterial culture after improved creamery methods, and the whole is chilled, granulated and churned. The subsequent working of the butter and packing for market is similar in all respects to the customary treatment.

It will be seen from the above description of the method of its preparation that renovated butter cannot be expected to vary greatly from ordinary butter in its chemical composition. The only differences must arise from the substitution of a different buttermilk for that originally present, and whatever changes have been brought about in the butter-fat by the manipulations to which it has been subjected. In the appended table I have brought together the average results of the analysis of 75 samples made in this laboratory during the first four months of the operation of the law. The samples were produced at licensed factories located in different parts of the United States, and were accompanied in most cases by affidavits of the producers to the effect that the samples fairly represented their product. In other cases they were taken by government officers.

The methods of analysis used were essentially those of the Association of Official Agricultural Chemists; the Reichert-Meissl value was determined strictly in accordance with Wollny's procedure, as officially prescribed by the English government.<sup>1</sup> The percentage of water was determined by difference and also by drying.

<sup>1</sup> *Analyst*, 25, 309 (1900).



direct. The latter is the figure used in passing upon the liability of the butter to tax as "adulterated butter," on account of containing an excessive quantity of "water, milk or cream." The regulations fix the maximum limit at 16 per cent., following European precedent in this respect.

TABLE OF AVERAGES.

Fat.	Per cent.	Curd.	Per cent.	Ash.	Per cent.	Water direct.	Per cent.	Water by differ-	ence.	Per cent.	Specific gravity at	Refractive index at	Reichert-Meissl	Valenta	Crismer	Acidity.	Iodine
82.05		1.47		2.85		14.44		14.42		0.9106	40°	23°	29.15	41.6°	49.05°	6.57	36.78

Of the above, the percentage composition figures and the refractive index and Reichert-Meissl value, represent the mean of all the samples; the specific gravity was determined upon fifty-eight only, the Crismer, Valenta and acidity values upon fifty-four, and the iodine value upon twenty-five.

The maximum percentage of fat in any sample was 88.88, the minimum, 68.80; curd, maximum, 2.65 and minimum, 0.77; ash, maximum, 7.49 and minimum, 0.97; maximum of water by direct determination, 23.17 and minimum, 8.01; maximum of specific gravity, 0.9124 and minimum, 0.9093; maximum refractive index, 1.4619 and minimum, 1.4600; the maximum Reichert-Meissl value, 31.82 and the minimum, 25.42. The highest Crismer value was 54.80°, the lowest, 43.2°; the highest Valenta value was 50°, the lowest, 33.5°; the highest acid figure was 13.40, the lowest, 1.72; the highest iodine value was 41.15, the lowest, 34.20.

Of particular interest was the water determination, in view of the definition of adulterated butter in the law. Eight of the samples gave results in excess of the maximum limit prescribed by the regulations, as shown by the following table:

On account of the heavy tax imposed upon the manufacturers of adulterated butter by the law, it is desirable that the product of renovated butter factories should be carefully controlled by the persons responsible for their operation, in order that it be kept well within the prescribed limit in content of water. The difficulties in the way of an accurate determination of this constituent in a fatty substance like butter are well known. These difficulties apply both to the sampling and to the determination

**ANALYSIS OF RENOVATED BUTTERS SHOWING A HIGHER CONTENT OF  
WATER THAN 16 PER CENT.**

Serial No.	Fat. Per cent.	Curd. Per cent.	Ash. Per cent.	Water direct. Per cent.	Water by difference. Per cent.	Specific gravity at 40°	Refractive index at 25°	Reichert-Meissl value.	Cramer value.	Valenta value.	Acidity.	Iodine value.
5735	75.64	1.73	2.95	20.62	19.68	0.9103	1.4605	30.99	48.8 °	42.0°	6.11	36.96
5795	77.12	0.77	0.97	20.32	21.14	0.9108	1.4603	30.13	47.68°	42.5°	7.30	34.70
5813	79.81	1.69	1.09	17.36	17.41	0.9112	1.4605	28.58	50.33°	38.5°	7.66	37.35
5877	78.34	1.52	2.83	18.01	17.31	0.9104	1.4617	26.52	49.68°	42.0°	6.04	....
5902	77.44	1.20	2.08	20.07	19.28	0.9112	1.4608	29.49	.....	.....	...	....
5995	79.60	1.73	2.36	16.74	16.31	0.9096	1.4917	26.53	.....	...	...	....
6006	68.80	2.47	6.29	23.17	22.44	.....	1.4613	28.48	.....	.....	...	....
6139	75.91	1.57	6.12	16.58	16.40	.....	1.4607	28.64	48.28°	40.0°	9.28	....

itself. While the average figures for the direct and indirect estimation as given above are in very close agreement, the table of analyses shows a very wide difference in both directions. In several samples, the percentages by the two different methods are over 1 per cent. apart, and one varies by 1.70 per cent. The direct estimation by drying was used in all cases in passing upon the classification of the butter.

**TESTS FOR RENOVATED BUTTER.**

The behavior of each sample under the different tests which have been suggested for the identification of renovated butter was studied. The tests used were: First, the appearance of the fat when viewed by polarized light (Brown-Taylor-Richards test for melted fat);<sup>1</sup> second, the behavior of the fat when boiled in an open vessel (generally known as the "spoon test"); and third, the granulation or "gathering" of the fat when cooled in milk (Waterhouse test).

These tests are described in the methods of the Association of Official Agricultural Chemists, and the last-named especially is quite fully discussed by Patrick, in the proceedings of the same association for 1901, p. 126, and made applicable to household conditions for detecting oleomargarine, in Farmer's Bulletin, No. 131, of the U. S. Department of Agriculture. Applied to the above known samples of renovated butter, all the tests failed to give positive results in one or more instances.

<sup>1</sup> See This Journal 22, 703 (1900).

No. 6044 did not respond to the Waterhouse test, and No. 5736 failed with the spoon test, while several of the samples did not give positive indications of melted fat under the microscope. Of the three, the Waterhouse test was found most reliable and definite in its indications. The principle of this test has been used by a recent writer as the basis of a quantitative separation of butter from oleomargarine.<sup>1</sup>

Hess and Doolittle<sup>2</sup> differentiate between fresh and renovated butter by the character of the curd. Their qualitative test, based upon the appearance of the separated curd, has given no satisfaction whatever in this laboratory; and no work has been done upon their quantitative distinction based upon the relation of casein to albumins.

#### EXPERIMENTS TO DETERMINE CHANGES BROUGHT ABOUT IN BUTTER-FAT BY AERATION.

Having in mind the very radical changes brought about in oils by the process of "blowing," or oxidation, I thought it would not be difficult to establish differences in the composition of butter-fat brought about by the aëration to which it is subjected in the process of renovation. Either because lower temperatures are maintained, however, or for other reasons, no decided changes appear to be produced, and the results of the few experiments I have been able to make in this direction are negative. I will detail them here, however, hoping the matter may be further investigated by others:

A sample of high-grade creamery butter was purchased early in the summer and a portion of it was subjected to analysis. It was then freely exposed to the atmosphere of the laboratory, and even inoculated with rancid butter to hasten its deterioration. It was kept under these conditions throughout the summer, about three months, at the end of which period it had greatly deteriorated, but was not nearly so rancid or offensive as might have been expected. A portion was again taken for analysis and the remainder was melted, and the fat subjected to the process of renovation, as nearly as it could be approximated in the laboratory. The aëration could not be very well carried out, however, and the final result was not very satisfactory, so far as the practical im-

<sup>1</sup> Deguide: *J. Pharm. Chim.*, 16, 372 (1902); *Abstr. J. Soc. Chem. Ind.*, 21, 1352 (1902).

<sup>2</sup> This Journal, 22, 150 (1900).

provement of the flavor of the fat was concerned. No attempt was made to rechurn the butter, and the last analysis was made upon the renovated fat. The results of the three analyses are given in the following table:

## SERIAL NO. 4975.

	Fresh.	After having become rancid.	After renovation.
Fat, per cent .....	88.81	88.70	....
Water, per cent.....	8.07	7.17	....
Curd, per cent.....	1.16	1.36	....
Ash, per cent.....	1.96	2.77	....
	100.00	100.00	....
Values for fat.			
Specific gravity at $\frac{40^{\circ}}{40^{\circ}}$ C .....	0.9106	0.9117	0.9117
Refractive index at $25^{\circ}$ C.....	1.4612	1.4613	1.4614
Reichert-Meissl value .....	27.97	27.27	27.46
Acid value, cc. normal alkali required for 100 grams fat.....	....	4.28	4.28
Hehner value.....	88.94	85.43	85.23
Valenta value.....	44.75°	49.°	48.°
Crismer value.....	58.5°	49.7°	49.7°
Saponification value.....	217.3	217.3	214.8
Soluble fatty acids, per cent .....	4.63	3.77	3.89

It will be seen that the fat values of the butter after renovation differ less from those of the butter before renovation than the latter differ from the values of the fresh butter.<sup>1</sup>

Through the courtesy of a firm of local manufacturers, an opportunity was offered to take samples of butter before and after renovation in the regular work of the factory. Two sets of samples were taken on two different days; it was not found possible to make the samples all strictly comparative on account of the difficulty of sampling the material in solid form, and for other reasons. The samples of butter-fat before and after blowing, however, are believed to be very closely comparable, having been taken from a single vessel containing a large quantity of the material, the one before, and the other after it had been subjected to the aerating process.

The following table gives the results obtained:

<sup>1</sup> Compare this Journal, 24, 711 (1902).

# RENOVATED BUTTER.

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Description of sample.	First Experiment.		Second Experiment.	
	Butter-fat, before blowing.	Butter-fat, after blowing.	Butter-fat, before blowing.	Butter-fat, after blowing.
Series No.	5636	5637	5644	5646
Fat. Per cent.	82.78	82.78	87.36	82.78
Curd. Per cent.	1.34	1.34	1.51	1.32
Ash. Per cent.	2.16	2.16	2.24	2.51
Water (direct determination).	0.20	0.08	8.18	0.05
Water (by difference).	13.72	13.72	8.89	13.39
Specific gravity at 40° C.	0.9103	0.9109	0.9097	0.9101
Refractive index at 25° C.	1.4607	1.4609	1.4606	1.4607
Acidity (cc. normal alkali required for 100 gms. fat).	7.32	7.28	3.98	9.11
Reichert-Meissl value.	28.86	29.73	28.56	28.38
Hehner value.	85.60	85.87	86.00	86.34
Valenta value.	44.0	43.0	46.0	43.0
Crismer value.	45.73	44.5	48.39	44.31
Iodine value.	37.38	36.50	37.09	36.76
Soluble acids. Per cent.	4.92	5.06	4.99	4.86

The greatest variation in any of the values obtained from the butter-fat is shown by the Reichert-Meissl value. In the first series of samples, the Reichert-Meissl value of the fat is higher after blowing than before, while in the second series it is just the reverse. I am unable to account for this. The variations in the other values are slight, and no definite conclusion can be drawn from them. Apparently the differences in the composition of butter-fat brought about by renovation, if any, are minute, and a long series of comparative analyses would be necessary to develop them.

For the present, reliance must be placed upon the physical tests for melted fat, as previously detailed.

I am indebted to Messrs. Simons, Adams, and Law, assistants in the laboratory, by whom the analytical work was performed.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

### ON SOME ALDEHYDE CONDENSATION PRODUCTS OF ARYLPSEUDOTHIOHYDANTOINS.

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

Received January 23, 1902.

IN the course of our<sup>1</sup> work on the molecular rearrangement of thiocyanacetanilides it was found that certain stable pseudothiohydantoins gave diacetyl derivatives when warmed with acetic anhydride, and it was shown that these acetyl compounds did not behave like acetoacetic acid derivatives. This would seem to indicate that the group  $\text{—CO—CH}_2\text{—S—}$  is not present in the stable pseudothiohydantoins.

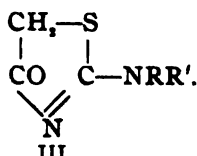
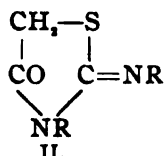
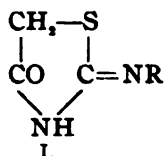
It has been shown, however, by Andreasch<sup>2</sup> that the non-substituted pseudothiohydantoin condenses with benzaldehyde and behaves like other<sup>3</sup> compounds which contain the above group; and we have now found that substituted pseudothiohydantoins, which are to be represented by formulas I, II and III, are also capable of condensing with aldehydes and with oxalic ester. The stable pseudothiohydantoins (I) therefore behave in a

<sup>1</sup> Wheeler and Johnson: *Am. Chem. J.*, 28, 121 (1902).

<sup>2</sup> *Monatsh. Chem.*, 8, 407.

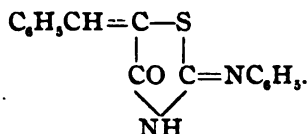
<sup>3</sup> Loven: *Ber. d. chem. Ges.*, 18, 3242 (1885); Nencki and Sieber: *Ibid.*, 17, 2278 (1884); Ginsberg and Bondzynski: *Ibid.*, 19, 119 (1886); *Monatsh. Chem.*, 8, 358 (1887); Andreasch: *Ibid.*, 8, 407, 10, 75 (1889).

tautomeric manner in regard to their reactions with acetic anhydride and aldehydes.



The condensation products which we have obtained vary in color from light yellow to deep red and have the properties of weak dyes; in this they resemble the corresponding products of rhodanic acid,  $\alpha$ - $\mu$ -diketotetrahydrothiazole, and the non-substituted pseudothiohydantoin with salicylic and cinnamic aldehydes which have been described by Andreasch and Zipser.<sup>1</sup>

*Benzaldehyde and Phenylpseudothiohydantoin,*



Ten grams of the stable phenylpseudothiohydantoin were dissolved in about 150 cc. of alcohol containing 1.2 grams of sodium. To this solution 5.3 grams of benzaldehyde were added and the mixture was heated for several hours. The alcohol was then evaporated, water and dilute acetic acid were added and, after thorough stirring, the yellow precipitate was filtered, washed and dried. The yield of this crude material corresponded with the theoretical. For analysis the substance was crystallized from alcohol and from amyl acetate, whereupon, minute, slender, light yellow prisms separated from both solvents. They melted at about 251°-252°, and a nitrogen determination gave:

	Calculated for $\text{C}_{16}\text{H}_{12}\text{ON}_2\text{S}$ .	Found.
Nitrogen.....	10.0	9.9

This compound or  $\alpha$ -keto- $\mu$ -phenylimido- $\beta$ -benzaltetrahydrothiazole is insoluble in water. It is fairly soluble in hot alcohol and it dissolves in hot dilute alkali but separates out again on cooling; it can be crystallized from dilute hydrochloric acid.

The *sodium ethylate addition product*,  $\text{C}_{16}\text{H}_{12}\text{ON}_2\text{S} \cdot \text{NaOC}_2\text{H}_5$ , is readily obtained by mixing the constituents in alcoholic solu-

<sup>1</sup> *Chem. Ztg.*, 26, 54, 623 (1902).

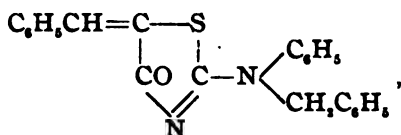
tion. It forms a bright yellow crystalline powder which melts at about  $263^{\circ}$ . Sodium determinations gave:

	Calculated for $C_{18}H_{17}O_2N_2SNa$ .	Found.	
		I.	II.
Sodium ...	6.6	6.5	6.3

The *silver salt*, prepared by dissolving the condensation product in alcoholic ammonia, forms a fine, yellow, crystalline powder. A silver determination gave:

	Calculated for $C_{18}H_{11}ON_2SAg$ .	Found.
Silver.....	27.9	28.2

*Benzalphenylbenzylpseudothiohydantoin*,

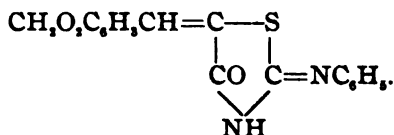


was obtained by heating the above sodium ethylate addition product with benzyl chloride in an alcoholic solution. Its structure was shown by the fact that the same compound results on condensing benzaldehyde with phenylbenzylpseudothiohydantoin. It crystallized from alcohol in bunches of very light yellow needles and melted at  $186^{\circ}$ - $187^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_{22}H_{19}ON_2S$ .	Found.
Nitrogen.....	7.5	7.7

This condensation product is insoluble in water and alkali; it dissolves readily in hot alcohol.

*Piperonalphenylpseudothiohydantoin*,



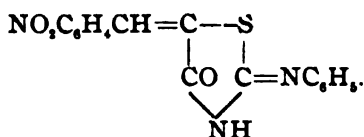
Three grams of phenylpseudothiohydantoin, 0.36 gram of sodium and 2.4 grams of piperonal were dissolved in alcohol and warmed for two hours. A bright yellow powder was thus obtained which, on crystallizing from alcohol, formed minute crystals melting at about  $259^{\circ}$ - $261^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_{17}H_{15}O_2N_2S$ .	Found.
Nitrogen.....	8.6	8.7



This material is difficultly soluble in alcohol and amyl acetate. It dissolves in glacial acetic acid and in hot alkali, but it is insoluble in water.

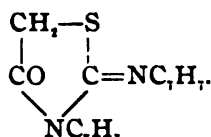
*Metanitrobenzalphenylpseudothiohydantoin*,



This was prepared in the same manner as the above. It was obtained as a dark brick-red crystalline powder which proved to be less soluble than the preceding compounds. For analysis it was purified by boiling with alcohol and dissolving in alkali, precipitating with acetic acid and then washing with water. Thus obtained it did not melt at  $290^\circ$  and a nitrogen determination gave:

	Calculated for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{S}$ .	Found.
Nitrogen.....	12.9	12.6

*Diorthotolylpseudothiohydantoin*,

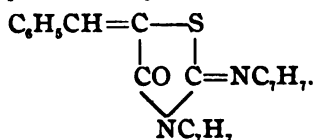


Fifty grams of diorthotolylthiourea and 20 grams of chloracetic acid were mixed in alcohol and the solution warmed for several hours. Upon cooling, colorless, flat prisms separated which, on crystallizing from alcohol, melted at  $151^\circ$ - $152^\circ$ , and a nitrogen determination gave:

	Calculated for $\text{C}_{17}\text{H}_{16}\text{ON}_2\text{S}$ .	Found.
Nitrogen.....	9.4	9.7

This hydantoin is readily soluble in alcohol and strong acetic acid but insoluble in alkali.

*Benzaldiorthotolylpseudothiohydantoin*,



This formed slender, light yellow prisms, when crystallized from alcohol, melting at  $179^{\circ}$ - $180^{\circ}$ . It is readily soluble in alcohol and insoluble in alkali. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}ON_4S$ .	Found.
Nitrogen.....	7.29	7.65

The *sodium ethylate addition product*,  $C_{24}H_{20}ON_2S.NaOC_2H_5$ , was obtained as a light yellow powder which did not melt at  $275^{\circ}$ . It was crystallized from alcohol and analyzed with the following results:

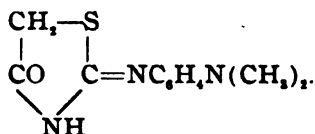
	Calculated for $C_{26}H_{22}O_2N_2SNa$ .	Found.	
		I.	II.
Nitrogen .....	6.19	6.21	6.13

*Paradimethylaminophenylthiourea*,  $H_2N-CS-NHC_6H_4N(CH_3)_2$ , was prepared from *p*-dimethylphenylene diamine hydrochloride and ammonium thiocyanate, in the usual manner. On crystallizing from alcohol, it formed a pale yellow powder which melted with effervescence at  $180^{\circ}$ - $181^{\circ}$ , giving a red liquid. A nitrogen determination gave:

	Calculated for $C_9H_{12}N_2S$ .	Found.
Nitrogen.....	21.53	21.38

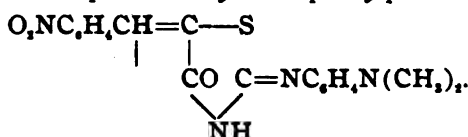
*Paradimethylaminophenylthiohydantoic acid*,  $HOCOCH_2S-C(NH)-NHC_6H_4N(CH_3)_2$ , was obtained from the above by warming with alcoholic ammonium chloracetate. It separated as a light yellow, insoluble powder.

*Paradimethylaminophenylpseudothiohydantoïn*,



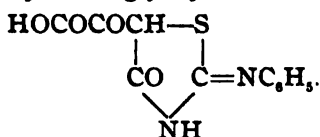
The above thiohydantoic acid was warmed with an excess of glacial acetic acid until solution took place. The acid was then neutralized with sodium carbonate and the precipitate was washed, dried and crystallized from alcohol. It formed a finely divided, dull yellow powder which sintered at about  $210^{\circ}$  and melted at  $222^{\circ}$ . A nitrogen determination gave:

	Calculated for $C_{11}H_{12}ON_2S$ .	Found.
Nitrogen.....	17.87	18.20

*Paranitrobenzalparadimethylaminophenylpseudothiohydantoin*,

Molecular quantities of paranitrobenzaldehyde, sodium ethylate and the above hydantoin were warmed for several hours in alcoholic solution. The alcohol was then evaporated and the residue was treated with water and acetic acid; the product was a deep red powder, insoluble in water and only slightly soluble in alcohol. For analysis it was boiled with water and alcohol. It then melted at about  $250^\circ$ - $252^\circ$  and a nitrogen determination gave:

	Calculated for $\text{C}_{16}\text{H}_{16}\text{O}_4\text{N}_4\text{S}$ .	Found.
Nitrogen .....	15.2	14.9

*Phenylpseudothiohydantoinglyoxylic acid*,

Ten grams of phenylpseudothiohydantoin, 1.2 grams of sodium, and 10 grams of ethyl oxalate were dissolved in alcohol and allowed to stand for two days. The solution was then heated to boiling for a few minutes and allowed to cool. The yellow sodium salt which separated was filtered and decomposed by dilute acetic acid. The product then crystallized from alcohol or amyl acetate in minute yellow crystals which melted, with effervescence, to a dark red liquid at about  $221^\circ$ - $222^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_2\text{S}$ .	Found.
Nitrogen .....	10.6	10.7

This acid is insoluble in water and difficultly soluble in alcohol. The *silver salt* was prepared by dissolving the acid in dilute alcoholic sodium hydroxide and adding silver nitrate. It formed a slate-colored amorphous precipitate which gave the following result on analysis:

	Calculated for $\text{C}_{11}\text{H}_8\text{O}_4\text{N}_2\text{SAg}_2$ .	Found.
Silver .....	45.1	45.2

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 76].

# THE SYNTHESIS OF ALKYLTHIOKETODIHYDROQUINAZOLINES FROM ANTHRANILICNITRILE.

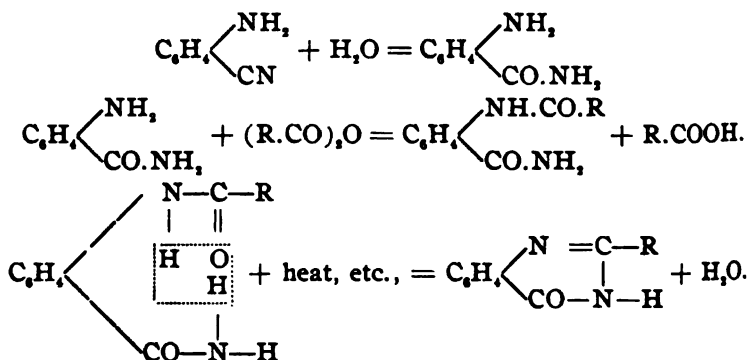
BY MARSTON T. BOGERT, H. C. BRENNEMAN, AND W. F. HAND.

Received February 16, 1903.

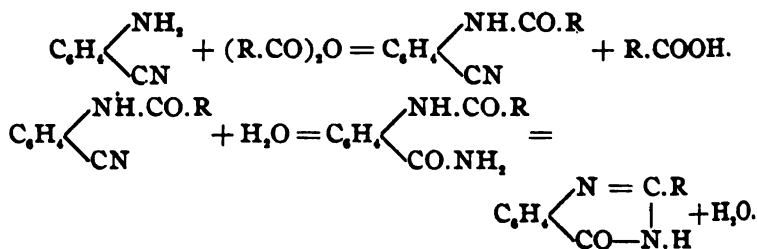
## THEORETICAL PART.

The methods for the production of alkylketodihydroquinazolines from anthranilicnitrile all depend upon the intermediate formation of acyl derivatives of anthranilamide, which then condense to the quinazoline by loss of water. In brief, these methods are as follows:

(1) Preparation of anthranilamide from the nitrile, conversion to an acyl derivative, and condensation of the latter by the action of heat, acids or alkalis, as worked out by Weddige and his students, by Niementowski and others:<sup>1</sup>



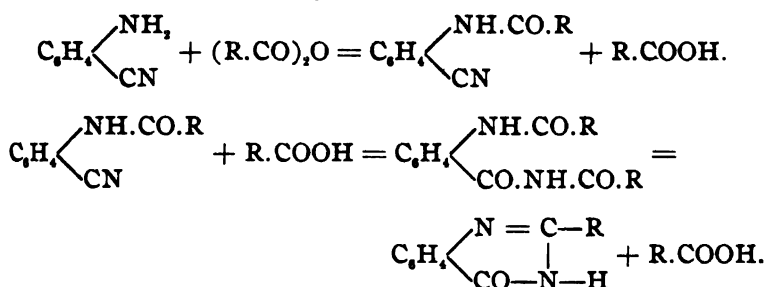
(2) By the action of warm alkaline hydrogen peroxide solution upon acylanthranelicnitriles:<sup>2</sup>



<sup>1</sup> Weddige: *J. prakt. Chem.* [2], 31, 124 (1885); 36, 141 (1887); Körner: *Ibid.*, 36, 155 (1887); Niementowski: *Ber. d. chem. Ges.*, 21, 1534 (1888), and *J. prakt. Chem.* [2], 40, 1 (1889); Knappe: *J. prakt. Chem.* [2], 43, 209 (1891); etc.

<sup>2</sup> Bogert and Hand: this Journal, 24, 1031 (1902).

(3) By heating anthranilicnitrile in sealed tubes with acid anhydrides:<sup>1</sup>



In (1) the amide is first formed and then acylated, in (2) the acyl group is introduced first and the nitrile then changed to the amide, while in (3) both reactions are accomplished in one operation, the amino group being the first point of attack.

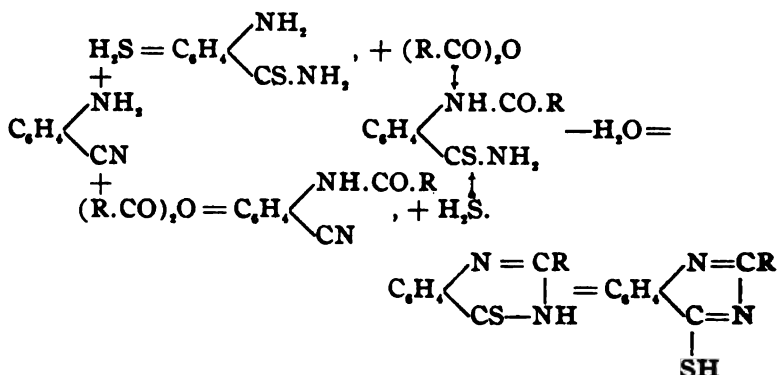
An examination of the reactions involved in methods (1) and (2) will immediately suggest to the reader, as it did to us, the possibility of preparing the corresponding thio derivatives by a similar series of reactions, in which the thiamide should be the intermediate product, instead of the oxygen amide. As the result of the practical testing in the laboratory of this idea, we are able to report the following new methods for the preparation of thioquinazoline derivatives:

(4) Anthranilic nitrile is converted to the thiamide by the direct addition of hydrogen sulphide, the thiamide acylated, and the acyl derivative then immediately condenses to the thioquinazoline by loss of water, the reactions involved being similar to those given under (1).

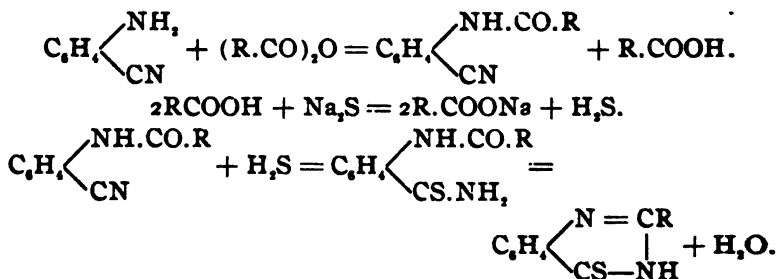
(5) The nitrile is first acylated, hydrogen sulphide then added to the cyanogen group, and the resulting acylthiamide condenses to the thioquinazoline as just noted, the reactions being similar to those given under (2).

The relation of methods (4) and (5) to one another appears clearly in the following diagram:

<sup>1</sup> Bogert and Hand: *Loc. cit.*

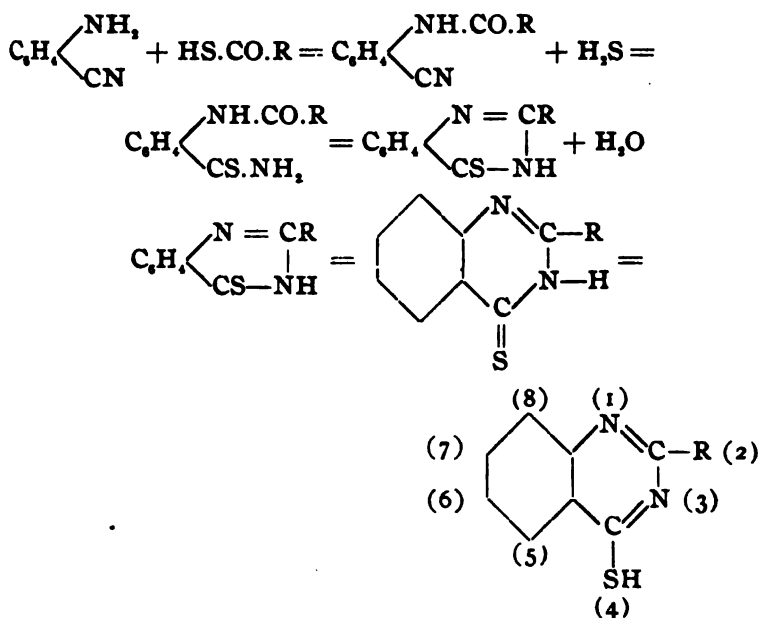


(6) The reactions involved in method (5) may be carried out practically simultaneously by treating the aminonitrile with an acid anhydride and sodium sulphide. The anhydride first acylates the amino group, the organic acid thus separated as the by-product liberates hydrogen sulphide from the sodium sulphide, this hydrogen sulphide attaches itself to the cyanogen, and the acyl thiamide thus produced condenses as usual to the thioquinazoline, the entire series of reactions being completed in one operation:

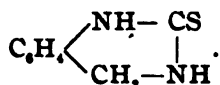


The sodium salt formed probably assists in some cases in the elimination of the water for the final condensation. This synthesis may be carried out in open flasks or in sealed tubes. So far, our results have been rather better with sealed tubes, and we have found it advantageous to use an excess of the sulphide.

(7) By the use of thio acids, in sealed tubes, the same results may be secured, likewise, in a single operation. The thio acid first acylates the amino group with liberation of hydrogen sulphide, and as this hydrogen sulphide cannot escape from the tube it attaches itself to the cyanogen, and the condensation already described then takes place:



The thioquinazolines obtained by these reactions belong to a different type from any hitherto recorded, in that they carry the sulphur atom upon the carbon adjacent to the benzene nucleus (*i. e.*, at position 4), while in those already known the sulphur is attached to the carbon between the two nitrogens (*i. e.*, at position 2), as in the following compound:<sup>1</sup>



In the preparation of the methyl, ethyl, normal and isopropyl derivatives by these methods, the condensation product invariably separated in beautiful golden yellow crystals which were quite easily purified, and the yield in several cases was nearly quantitative.

#### EXPERIMENTAL PART.

*o*-Aminobenzthiamide,  $\text{H}_2\text{NC}_6\text{H}_4\text{CSNH}_2$ .—This was prepared by placing anthranilicnitrile in a strong glass tube, adding alcohol which had been previously saturated at  $0^\circ$  with dry ammonia and

<sup>1</sup> Compare Stewart: *J. prakt. Chem.*, [2], 44, 415 (1891); Busch: *Ber. d. chem. Ges.*, 25, 2853 (1892); Paal and Commerell: *Ibid.*, 27, 1866, 2427 (1894); Paal and Vanvoixem: *Ibid.*, 27, 2413 (1894); Busch and Brunner: *J. prakt. Chem.*, [2], 82, 373 (1895); etc.

dry hydrogen sulphide, sealing the tube and heating at  $100^{\circ}$  for several hours. Generally, the thiamide crystallized out as the tube cooled. The crystals thus obtained, if washed with ether, to remove unchanged nitrile, and recrystallized from alcohol, were quite pure. Where no crystals separated in the tube, evaporation of the alcoholic solution gave large yellowish cubical crystals of the thiamide, which melted quite sharply at  $120^{\circ}$ , and yet which contained considerable free sulphur, as shown by check analyses. These crystals, when dried, carefully washed with carbon bisulphide (in which the thiamide is also partly soluble) and recrystallized from water, melted at  $121^{\circ}$ - $122^{\circ}$ . The thiamide may be precipitated from its concentrated alcoholic solution by the addition of chloroform; or, by adding water, the thiamide and nitrile may be precipitated together and the nitrile removed from the dried precipitate by washing with chloroform, the residue being purified by recrystallization from water.

The pure thiamide crystallizes in beautiful, light yellow flakes or plates, or occasionally in cubical crystals, melting-point  $121^{\circ}$ - $122^{\circ}$ . It is difficultly soluble in water, ether or chloroform in the cold, moderately soluble in the same solvents when boiling, and soluble in alcohol or carbon bisulphide. The substance softens under boiling water. Some of the purified product was analyzed, with the following results:

	Calculated for $C_6H_7N_2S$	Found.				
		I.	II.	III.	IV.	V.
Carbon.....	55.260	55.36	....	....	....	....
Hydrogen.....	5.263	5.31	....	....	....	....
Nitrogen.....	18.425	...	18.65	18.55	...	....
Sulphur.....	21.052	...	....	....	20.81	20.76

Analysis (I) was made with crystals which had been precipitated from alcoholic solution by chloroform and subsequently purified; analyses (II), (III), (IV) and (V) were made with crystals which separated in the tube and were purified by washing with ether and recrystallizing.

The thiamide can also be prepared at ordinary pressure, but we have not found the yield so good as when the reaction is carried out in sealed tubes.





*From o-Aminobenzthiamide and Acetic Anhydride.*—The thiamide was boiled gently for some time with acetic anhydride, and the thioquinazoline produced purified by crystallization from dilute alcohol. The yield was not very good.

*From Acetylanthranilicnitrile and Hydrogen Sulphide.*—The nitrile was heated in sealed tubes at  $100^{\circ}$  with alcohol saturated at  $0^{\circ}$  with hydrogen sulphide and containing a little ammonia. The thioquinazoline crystallized out in the tubes, on cooling, and was purified by crystallization from 20 per cent. alcohol. The yield was good. The same synthesis was accomplished by heating in an open flask, but the yield was less satisfactory.

*From Anthranilicnitrile, Acetic Anhydride and Sodium Sulphide.*—By heating these substances together in sealed tubes for an hour and a half at  $100^{\circ}$ - $110^{\circ}$ , the condensation product was obtained in beautiful crystals and in good yield: The contents of the tube were dissolved in dilute sodium hydroxide solution, the thioquinazoline precipitated by a current of carbon dioxide, and the precipitate purified by recrystallization from dilute alcohol. The tubes should not be heated much above  $110^{\circ}$ , or decomposition is likely to set in. This condensation was also carried out in an open flask. On mixing the substances, heat was developed, but very little hydrogen sulphide escaped. After heating for an hour and a half, the mixture in the flask set to a mass of yellow crystals. These were washed with cold water and purified as before.

*From Anthranilicnitrile and Thiactic Acid.*—When these substances were heated together in sealed tubes the yield of thioquinazoline was rarely less than 80 per cent. of the theoretical and frequently approached quantitative results. The condensation product separated in the tubes in crystals which were practically pure.

*Properties of 2-Methyl-4-thioketodihydroquinazoline.*—The product obtained from the above reactions crystallizes from dilute alcohol in beautiful, long, yellowish needles or prisms, melting at about  $218^{\circ}$ - $219^{\circ}$  with decomposition; by careful heating, it may be sublimed, and then shows a slightly higher melting-point. It dissolves readily in alkalis or in hot alcohol, and is slightly soluble in water, ether, chloroform or benzene, when hot. Some of the purified product from the action of hydrogen sulphide upon acetylanthranilicnitrile was analyzed, with the following results:

	Calculated for $C_9H_7SN_2$	Found.		
		I.	II.	III.
Carbon .....	61.364	61.29	....	....
Hydrogen .....	4.546	4.71	....	....
Nitrogen .....	15.909	....	15.93	15.96
Sulphur .....	13.181	....	....	....

The *picrate* forms large, light yellow needles, melting at  $198.5^\circ$ - $199.5^\circ$ , and is moderately soluble in cold water, more readily in hot water or in dilute alcohol, easily soluble in 95 per cent. alcohol.

#### *2-Ethyl-4-thioketodihydroquinazoline.*

*From o-Aminobenzthiamide and Propionic Anhydride.*—The thiamide was placed in a strong, glass tube and treated with a slight excess of propionic anhydride. Considerable heat was developed, and as the temperature rose the amide was thereby completely dissolved. On cooling down, the product separated upon the sides of the tube in small rose-like masses, the contents soon entirely solidifying. The tube was then heated for an hour and a half at  $110^\circ$ - $115^\circ$ , when light yellow, cubical crystals separated upon cooling, which were washed with dilute alcohol and dried, and then appeared to be the pure thioquinazoline.

*From Propionylanthranilicnitrile and Hydrogen Sulphide.*—The nitrile was dissolved in alcohol, the solution saturated with dry hydrogen sulphide and dry ammonia, and heated at  $156^\circ$  for sixteen hours. The contents of the tube were then dissolved in warm dilute sodium hydroxide solution, the thioquinazoline precipitated by a current of carbon dioxide and purified by crystallization from dilute alcohol.

*From Anthranilicnitrile, Propionic Anhydride and Sodium Sulphide.*—By heating these substances together in sealed tubes for seven hours at  $165^\circ$ - $170^\circ$ , the thioquinazoline is produced and crystallizes out upon cooling. It was purified as described above. The same condensation can be secured by heating the mixture in an open flask at  $100^\circ$ - $125^\circ$ , the cake of crude crystals thus obtained being purified in the usual manner. A rather higher temperature and longer heating is necessary than in the case of the methyl derivative.

*Properties of the 2-Ethyl-4-thioketodihydroquinazoline.*—The ethyl derivative forms yellowish needles, melting at about  $203^\circ$ .

204° with decomposition. By careful heating, it may be sublimed in needles, which show a somewhat lower melting-point (200.5°-201.5°). It is apparently insoluble in cold water, moderately soluble in dilute alcohol or in carbon tetrachloride, soluble in alcohol, aniline, benzene, or in caustic alkalies. The purified substance from the sodium sulphide method was analyzed, with the following results:

	Calculated for $C_{16}H_{10}SN_2$ .	Found.			
		I.	II.	III.	IV.
Carbon .....	63.158	63.79	....	....	....
Hydrogen.....	5.263	5.34	....	....	....
Nitrogen.....	14.737	....	14.93	14.90	....
Sulphur.....	16.842	....	....	....	17.50

The material used in (IV) consisted of crystals taken direct from one of the tubes, washed and dried, but not further purified. It shows, as expected, slight contamination with free sulphur.

The *picrate* crystallizes in coarse needles.

*2-Isopropyl-4-thioketodihydroquinazoline.*

Anthranilicnitrile, isobutyric anhydride and sodium sulphide, were heated together in sealed tubes for from three to six hours at 170°-175°, and the product purified by dissolving in sodium hydroxide solution, precipitating with carbon dioxide and crystallizing the precipitate from alcohol. Long warming with dilute alkali appears to induce partial decomposition with separation of gummy substances, so that the alkaline solution should be precipitated by the carbon dioxide without undue delay. The pure substance crystallizes from alcohol in long, light yellow needles, melting-point 203°-204°. It will be observed that this melting-point is identical with the melting-point of the ethyl derivative.

*2-Normal Propyl-4-thioketodihydroquinazoline.*

Anthranilicnitrile, *n*-butyric anhydride and sodium sulphide were heated together in sealed tubes for eight hours at 182°, and the condensation product purified as described for the isopropyl derivative. It forms beautiful, light yellow needles, melting at 182°-183°, which can be sublimed by careful heating.

It is rather interesting to note that the melting-point of these thioquinazolines steadily sinks with increasing molecular weight, the iso-compounds melting higher than those with normal structure. We have already called attention in previous papers to a

similar condition of affairs in the case of the corresponding oxygen alkylketodihydroquinazolines and in the acylanthranilic nitriles. The solubility, however, diminishes with increasing molecular weight.

All melting-points recorded in this paper were determined with Anschütz short-scale thermometers, standardized by the Reichs-Anstalt, the entire mercury column being immersed in the heating medium.

The work is being continued.

ORGANIC LABORATORY, HAVEMEYER HALL,  
COLUMBIA UNIVERSITY, January 31, 1903.

### ACTION OF METALLIC MAGNESIUM UPON AQUEOUS SOLUTIONS<sup>1</sup>.

BY LOUIS KAHLENBERG.

Received January 31, 1903.

It has long been known that metallic magnesium acts extremely slowly upon distilled water, and that it practically does not act at all upon solutions of the caustic alkalis. In 1899 Tommasi<sup>2</sup> made qualitative investigations of the action of magnesium on aqueous solutions of the following salts: KCl, NH<sub>4</sub>Cl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, NaCl, LiCl, BaCl<sub>2</sub>, SrCl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>Cl, CdCl<sub>2</sub>, PbCl<sub>2</sub>, HgCl<sub>2</sub>, FeCl<sub>3</sub>, CrCl<sub>3</sub>, PtCl<sub>4</sub>, AuCl<sub>3</sub>, CuSO<sub>4</sub>, ZnSO<sub>4</sub>, FeSO<sub>4</sub>, MnSO<sub>4</sub>. He found that from solutions of sodium, potassium and lithium chloride, magnesium liberates hydrogen more rapidly than from pure water, magnesium hydroxide being formed. Solutions of the chlorides of barium, strontium, and calcium were acted upon but feebly by magnesium, but ammonium chloride solution was attacked at a lively rate. From solutions of the salts of the heavy metals mentioned above, hydrogen was liberated by magnesium, the chloride or sulphate of that metal being formed, and a basic salt or hydroxide of the heavy metal, or the latter in the metallic state, precipitated. No theoretical explanations were attempted. In the same year G. Lemoine<sup>3</sup> called particular attention to the action of magnesium upon aqueous solutions of magnesium salts. He used solutions of the nitrate, chloride, sulphate and acetate of magnesium, but worked especially with the last three salts. From

<sup>1</sup> Read at the Washington meeting of the American Chemical Society, and at the meeting of the Wisconsin Academy of Sciences, Arts and Letters at Madison, December 26, 1902.

<sup>2</sup> *Bull. Soc. Chim.*, (3) 21, 885-887 (1899).

<sup>3</sup> *Compt. Rend.*, 29, 291 (1899).

aqueous solutions of these salts, magnesium liberates hydrogen rapidly and continuously. Using magnesium in form of powder, he found that about 0.4, the calculated amount of hydrogen, was liberated from a magnesium chloride solution when the powder was present in excess, the action being finally checked by the accumulation of the precipitate formed; but up to the maximum, the quantity of hydrogen disengaged was nearly proportional to the amount of magnesium added. After magnesium had acted upon the solutions of the chloride and acetate, these were found to contain but a relatively slight excess of the base. The analytical data show that the precipitates formed were very basic chloride and acetate of magnesium respectively. In the case of the magnesium sulphate the solution was much weaker after the magnesium had acted upon it, a very considerable portion of the salt having been thrown down in combination with the magnesium hydroxide in form of a basic sulphate of magnesium. Lemoine's explanation of the action of magnesium on solutions of magnesium salts is that in these solutions the salts are slightly decomposed into magnesium hydroxide and free acid. This acid acts on the metal, forming hydrogen and a basic salt which breaks up into the normal salt and hydroxide of magnesium; the latter finally drops out of solution and the reaction begins anew. In advancing this explanation it would certainly seem that Lemoine did not give due weight to the fact that the reaction of the solutions of the magnesium salts toward indicators is perfectly neutral at the outset, and that soon after introducing the magnesium it becomes alkaline and remains so, while the liberation of hydrogen continues unabated. There are thus no facts upon which to base the assumption that the salts he used are even slightly decomposed by water into free acid and magnesium hydroxide.

H. Mouraour<sup>1</sup> again directed attention to the fact that magnesium liberates hydrogen readily not only from solutions of its own salts, but from solutions of other salts as well. He found solutions of the carbonate, chloride, oxalate and sulphide of ammonium strongly acted upon; but no action was observed in the case of a solution of ammonium fluoride. Sodium carbonate, acetate and tetraborate solutions were strongly acted upon, as were also solutions of ordinary and chrome alum. On the other hand, the action

<sup>1</sup> *Compt. Rend.*, 130, 140 (1900).

was feeble on solutions of sodium phosphate, nitrite, thiosulphate, potassium ferrocyanide and the chlorides of barium, calcium and potassium. The work was entirely qualitative in character. Mouraour states that while Lemoine's explanation of the action may hold good in the case of solutions of chloride of magnesium, for instance, for the most of the salts last mentioned it is inadequate. In the case of the ammonium salts, Mouraour ascribes the action to the fact that solutions of these salts dissolve magnesium hydroxide. But he states that in the case of the salts of lead, copper, mercury and cobalt, from which magnesium precipitates the heavy metals and simultaneously liberates hydrogen, we have a secondary action of the magnesium on the water of the solution. He deems it very difficult to explain the phenomena in the cases last mentioned, stating that it is not probable that salts of these heavy metals favor the solubility of magnesia. Mouraour was apparently not aware of the work of Tommasi. As a matter of fact, magnesium hydroxide is not formed at all when solutions of the heavy metals named are acted upon by magnesium; the salt of the latter metal forms and remains dissolved, the basic salt or hydroxide of the heavy metal being precipitated. In fact, the cases which Mouraour finds difficult to explain are really most readily explained, for the salts of the heavy metals are indeed slightly decomposed by water, a small quantity of free acid being liberated as the acid reaction of such solutions clearly shows. This acid acts on the magnesium, evolving hydrogen and forming the corresponding magnesium salt, a basic salt or hydroxide of the heavy metal resulting simultaneously.

In presenting to my students the various ideas that have from time to time been entertained by scientific men regarding the nature of solutions, I have always laid considerable stress upon the view that the process of solution depends upon a mutual interaction of solvent and solute, and that solutions are chemical combinations<sup>1</sup> of solvent and solute according to variable proportions. Although this view has of recent years been relegated to the background by many, it certainly has a formidable array of facts to support it; and such facts have really been accumulating more and more, though the investigations yielding them have been guided to a considerable extent by the analogy between gases and solutions.

<sup>1</sup> Compare Mendeleeff: "Principles of Chemistry," Vol. I; Pickering, on solutions, Watts' "Chemical Dictionary;" Horstmann, Graham-Otto: "Lehrbuch der Physikalischen und Theoretischen Chemie," Vol. II.

If when a substance is dissolved in water chemical combination between that substance and water takes place, the liberation of hydrogen from the solution ought to result with a different degree of readiness than from pure water. With this as the guiding idea, Mr. O. W. Brown and Dr. H. V. Black at my suggestion made some preliminary experiments in this laboratory last summer, comparing the rate with which hydrogen is evolved from various aqueous solutions by the action of magnesium upon them. In the course of these experiments (among which many of the observations of the above named French investigators were confirmed, though at the time their researches had not been looked up) it was found that hydrogen was liberated with different rapidity in the case of each solution tested, and that this rate was different from that observed when pure water was used. To my regret Messrs. Brown and Black were unable to continue these investigations, much as they were inclined to do so. It seemed to me well worth while to follow out somewhat further the work thus begun, and the results obtained in investigating the subject will now be presented.

The metallic magnesium used was of Schuchardt's manufacture. It was carefully tested and was found to be free from carbon, and from alkali and alkaline earth metals. 0.8593 gram of the metal yielded 0.0036 gram of the mixed sesquioxides of iron and aluminum. Other metals were not present in the magnesium. The latter was cut into bars of square cross-section measuring 5 mm. on an edge, and having a length of 57.5 mm., thus presenting a surface of 1200 sq. mm. A large number of such bars was prepared. In each liquid to be tested, such a bar was immersed, its surface being first carefully cleaned with fine emery cloth. The action of the metal upon the liquid was noted and the volume of hydrogen evolved at different times was observed. The experiments were conducted at room temperature which was nearly 20°. The ordinary distilled water of the laboratory was used. The chemicals were either of Kahlbaum's or Schuchardt's manufacture; they were tested as to their purity, special care being taken to see that they were free from traces of heavy metals, and in the case of the salts employed, that they were perfectly neutral. Although only one series of results will be given in each case, each series was checked by at least one additional independent series. In the tables that follow, the first

column indicates the solute employed; the heading of each succeeding column indicates the time that a bar of magnesium acted upon the solution in order to liberate the volume of hydrogen given in that column.

TABLE I.

(Solutions contain 2 gram-mols. per liter, except the mannite and sodium sulphate solutions, which contain 1 gram-mol. per liter.)

Solute.	2.5 hours. cc.	23.5 hours. cc.	47.5 hours. cc.	53 hours. cc.
Distilled water (alone).....	0.02	0.10	1.5	1.8
Alcohol.....	0.10	0.40	7.6	7.8
Glycerin.....	0.01	0.05	0.5	0.55
Cane-sugar .....	0.10	0.65	1.0	1.2
Mannite .....	0.08	0.20	0.4	0.55
Urea .....	1.2	10.6	29.0	31.0
Sodium chloride .....	7.4	49.8	(discontinued) <sup>1</sup>	
Sodium sulphate .....	2.4	9.9	18.0	18.8

In the case of the urea solution, ammonia as well as hydrogen was liberated. When sodium nitrate solution is treated with magnesium, only a slight amount of hydrogen is actually evolved; this is due to the fact that the salt is reduced to nitrite. From a solution of ammonium chloride containing 2 gram-mols per liter, over 50 cc. of gas, consisting of hydrogen and ammonia, were liberated by one of the bars of magnesium in five minutes.

TABLE II.

(Solutions contain 1 gram-mol. per liter.)

Solute.	25 min. cc.	40 min. cc.	50 min. cc.	1 hr. cc.	1 hr., 20 min. cc.	1 hr., 35 min. cc.	2 hrs., 56 min. cc.	4 hrs., 23 min. cc.
MgCl <sub>2</sub> ...	13.0	18.5	22.0	24.8	30.5	33.8	(discontinued)	
MgBr <sub>2</sub> .....	4.8	7.0	8.5	9.9	13.0	14.8	24.5	33.4
MgSO <sub>4</sub> .....	5.9	9.4	11.6	13.75	18.5	21.5	36.4	50.5
Mg(NO <sub>3</sub> ) <sub>2</sub> ..	0.2	0.35	0.4	0.45	0.6	0.65	1.2	1.6

TABLE III.

(Solutions contain 1/10 gram-mol. per liter.)

Solute.	25 min. cc.	35 min. cc.	3 hrs., 31 min. cc.	4 hrs., 5 min. cc.	5 hrs., 32 min. cc.	22 hrs., 34 min. cc.
MgCl <sub>2</sub> .....	10.8	14.0	43.1	47.6	(discontinued)	
MgBr <sub>2</sub> .....	1.8	2.4	7.9	8.6	10.3	25.0
MgSO <sub>4</sub> .....	1.8	2.4	7.9	8.6	10.3	27.0
Mg(NO <sub>3</sub> ) <sub>2</sub> ..	0.2	0.3	1.7	1.8	2.2	3.6

<sup>1</sup> The word "discontinued" when used in the tables means that the experiment was discontinued, not that the hydrogen ceased to be evolved. The experiments in these cases had to be stopped because more gas could not be held in the tube used.



TABLE IV.

(Solutions contain 1/100 gram-mol. per liter.)

Solute.	17 min. cc.	31 min. cc.	45 min. cc.	49 min. cc.	2 hrs., 25 min. cc.	3 hrs., 37 min. cc.	5 hrs., 25 min. cc.	22 hrs., 49 min. cc.
MgCl <sub>2</sub> ....	1.8	3.2	4.7	5.2	12.2	15.6	20.0	43.0
MgBr <sub>2</sub> ...	1.4	2.0	2.6	2.8	5.8	7.1	9.6	20.9
MgSO <sub>4</sub> ...	1.5	2.4	3.0	3.2	6.8	8.8	11.6	29.6

TABLE V.

(Solutions contain 1 gram-mol. per liter.)

Solute.	17 min. cc.	31 min. cc.	45 min. cc.	49 min. cc.
KCl.....	11.5	17.5	22.5	24.0
KCl + MgCl <sub>2</sub> .....	15.0	23.0	29.4	31.4

TABLE VI.

(Solutions contain 1/10 gram-equivalent per liter.)

Solute.	2 min. cc.	4 min. cc.	6 min. cc.	11 min. cc.	16 min. cc.	26 min. cc.	33 min. cc.	36 min. cc.	46 min. cc.
H <sub>2</sub> SO <sub>4</sub>	3.2	8.0	12.0	21.0	28.0	37.6	40.4	41.8	45.6
Solute.	1 min. cc.	3 min. cc.	5 min. cc.	7 min. cc.	11 min. cc.	14 min. cc.	24 min. cc.	29 min. cc.	49 min. cc.
HCl..	3.0	8.5	14.0	19.0	27.5	31.4	39.4	43.5	48.8

(Solutions contain 1/100 gram-equivalent per liter.)

	5 min. cc.	10 min. cc.	17 min. cc.	20 min. cc.	30 min. cc.	40 min. cc.	1 hr., 5 min. cc.	1 hr., 20 min. cc.	3 hrs., 37 min. cc.
H <sub>2</sub> SO <sub>4</sub> 0.4	1.2	2.0	2.5	3.6	4.6	7.0	8.4	14.3	
HCl.. 0.4	1.2	2.0	2.5	3.6	4.7	7.0	8.0	11.8	

It was found that in normal potassium or sodium hydroxide solutions no measurable amount of hydrogen was evolved in twenty-four hours, the magnesium remaining perfectly bright. Solutions of magnesium nitrate when treated with magnesium yield nitrite and finally ammonia, which accounts for the small amount of hydrogen liberated by this salt as compared with other salts of magnesium. From solutions of magnesium acetate and iodide, magnesium also evolves hydrogen rapidly. A magnesium sulphate solution was treated with a large excess of finely divided magnesium, but no reduction of the salt to sulphite took place. From a solution of crystals of MgCl<sub>2</sub> + 6H<sub>2</sub>O in glycerin of 1.27 sp. gr., magnesium evolves hydrogen; the action is much increased upon heating. Anhydrous magnesium chloride (prepared from the double magnesium ammonium chloride) dissolved in glycerin of 1.27 sp. gr. acts slowly on magnesium; this action is greatly increased upon raising the temperature. The glycerin itself acts only very slightly on magnesium even on heating.

From  $\text{MgCl}_2 + 6\text{H}_2\text{O}$  melted in its crystal water, magnesium evolves hydrogen readily. A saturated solution of  $\text{MgCl}_2 + 6\text{H}_2\text{O}$  in ether does not attack magnesium. From a solution of 1 gram-mol.  $\text{MgCl}_2 + 6\text{H}_2\text{O}$  in 99.5 per cent. alcohol a bar of magnesium, of the size above described, evolved 2.5 cc. hydrogen in twenty-three hours and forty-seven minutes, while from 99.5 per cent. alcohol alone a like bar of magnesium liberated 0.9 cc. gas in twenty hours and forty-four minutes. Table I shows that from distilled water there was evolved under like conditions only 0.1 cc. in twenty-three and a half hours.

The results in Table I show that during the first twenty-three and a half hours all the solutions except that of glycerin act more vigorously on magnesium than on water alone. Throughout the experiment the glycerin solution lags behind water. After forty-seven and a half hours, more gas has been evolved from the water than from the solutions of glycerin, sugar and mannite, and the same holds true after fifty-three hours. It is especially interesting to note that the alcohol solution is much more vigorous in its action on magnesium than is pure water. The urea solution is relatively vigorously attacked, though, as has been stated, ammonia is also formed in this case. Again, sodium chloride solution is much more vigorous in its action than sodium sulphate solution of equivalent strength.

Tables II, III, and IV show that magnesium evolves hydrogen from solutions of magnesium salts at a fairly rapid rate. The solutions of the magnesium chloride are the most vigorously attacked in all cases. In the solutions containing 1 gram-mol per liter (Table II) the sulphate solution is acted upon more vigorously than that of the bromide; in the solutions containing 0.1 gram-mol per liter (Table III) hydrogen is evolved from the bromide and sulphate solutions at an equal rate for about five hours, within the limits of experimental error, while in the solutions containing 0.01 gram-mol per liter (Table IV) hydrogen is again evolved more rapidly from the sulphate solution than from that of the bromide. In the solution of nitrate of magnesium, nitrite is formed, as mentioned above, which accounts for the fact that but little gas appears in the case of this salt. Table V shows that the potassium chloride solution containing 1 gram-mol per liter acts fully as vigorously as a magnesium chloride solution of 1 gram-mol per liter. The double potassium magnesium chloride

acts still more strongly, as the table indicates. The observation that potassium chloride solutions act readily on magnesium agrees with that of Tommasi; Mouraour called the action feeble.

At my request, Mr. W. R. Mott measured the so-called single differences of potential between magnesium and some of the salt solutions in question. The measurements were made against the normal calomel electrode, the potential of which was taken to be  $-0.56$  volt. He found that at  $20^{\circ}$  C. the single potential between magnesium and sodium chloride solution (2 gram-mols per liter) is  $+1.163$  volts; between magnesium and sodium hydroxide (1 gram-mol per liter)  $+1.111$  volts, between magnesium and potassium hydroxide (1 gram-mol per liter)  $+1.140$  volts; between magnesium and potassium hydroxide (0.1 gram-mol per liter)  $1.105$  volts; and between magnesium and magnesium sulphate (1 gram-mol per liter)  $+1.366$  volts. Each result represents the average of four determinations in which different bars of magnesium were used. In the sodium chloride solution, the electromotive force changes but slightly with the time; in the caustic alkali solutions, the electromotive force tends to fall with lapse of time, while in the magnesium sulphate solution the electromotive force increases on standing.

The explanation of the above-described phenomena of the action of metallic magnesium upon aqueous solutions will now be considered. In the case of the saline solutions, one might feel inclined to assume that the salt acts upon the water liberating a certain amount of free acid which attacks the magnesium, resulting in the liberation of hydrogen and the formation of a normal or basic salt or hydroxide of magnesium, according to the nature of the solution under treatment.<sup>1</sup> This would be an attempt to extend Lemoine's interpretation of the action of magnesium upon aqueous solutions of its salts to all aqueous saline solutions. As stated above, there is ground for this explanation in the case of salts of the heavy metals, whose aqueous solutions, as is well known, have acid reactions indicating that they are indeed slightly decomposed by water yielding free acid. But in the case of salts

<sup>1</sup> In the language of the dissociation theory, preferred by some, it would mean that in saline aqueous solutions from which magnesium liberates hydrogen more readily than from pure water, the salt reacts upon the water slightly liberating some free acid, which in turn is electrolytically dissociated, yielding free hydrogen ions. The concentration of hydrogen ions in such solutions would then be greater than in pure water (which is supposed to be only slightly electrolytically dissociated) and this would account for the more vigorous action of magnesium upon saline solutions.

of Mg, Ca, Ba, Sr, K, Na, Li, there is no experimental evidence upon which to base the assumption that in their aqueous solutions there is any free acid present. Moreover an alkaline reaction is imparted to the solutions of these salts by the magnesium soon after it has been immersed in them, and yet this alkalinity does not interfere with the evolution of hydrogen.<sup>1</sup>

There are no facts upon which to base the assumption that magnesium chloride in aqueous solution suffers greater hydrolytic decomposition (of which free hydrochloric acid is one of the products) than do the chlorides of calcium, barium and strontium for instance; and yet solutions of the last three salts are acted upon but feebly by magnesium, while from the magnesium chloride solution hydrogen is rapidly evolved. This point is illustrated still more strikingly by the fact that solutions of sodium and potassium chlorides are relatively strongly attacked by magnesium; what reasons are there to assume that these salts are decomposed more by water than those of the alkaline earth metals? And again, would it be rational to suppose that because potassium chloride solutions attack magnesium more readily than sodium chloride solutions, the former salt is decomposed more by water than the latter? But the difficulty of this mode of explanation becomes even greater in the case of the non-saline solutions. So for instance the alcoholic solution is acted upon more vigorously than pure water; clearly there is no chance for assuming free acid to be the active agent in the case of this solution.<sup>2</sup>

The idea that Mouraour advances in the case of solutions of ammonium salts, namely, that the solubility of magnesium hydroxide in them determines the liberation of hydrogen from them by action of magnesium, might possibly be applied to other solutions and so the attempt be made to generalize this explanation. In addition to the ammonium salts, there are several cases that might be considered to favor this view. So magnesium hydroxide is less soluble in solutions of sodium and potassium hydroxide

<sup>1</sup> According to the dissociation theory, such an alkaline solution would contain fewer hydrogen ions than pure water, and yet hydrogen is evolved faster from them than from water.

<sup>2</sup> Indeed from the standpoint of the dissociation theory one would have to hold that the alcohol solution contains fewer hydrogen ions than are present in pure water, and hence action ought to be less than in the latter. Moreover from the point of view of this theory, magnesium ought to act rather less on solutions of magnesium salts, for the presence of magnesium ions would militate against the formation of more of them. And again, the difference of potential between magnesium and a magnesium sulphate solution ought to be less than between magnesium and a sodium chloride solution; the facts show that just the opposite is true.

than in pure water, and the fact that these solutions do not attack the metal as much as does water might be regarded as a support for the view advanced. Again, since ammonium fluoride solution is not acted upon by magnesium, and since the hydroxide and the fluoride of magnesium are insoluble in a solution of ammonium fluoride, this might be urged as another striking instance of the same kind. It would, however, be a delusion to think that the insolubility of magnesium hydroxide in these solutions is what prevents the magnesium from acting upon them. This becomes evident from the following experiment. On making magnesium amalgam (by heating magnesium and mercury together) and treating normal solutions of potassium and sodium hydroxide with the same, I found that hydrogen is very rapidly evolved, magnesium hydroxide formed, and mercury set free from the amalgam. Solution of ammonium fluoride is also violently attacked by magnesium amalgam with the concomitant liberation of hydrogen. Mere contact of magnesium and mercury in these solutions will not bring about this action, the amalgam must be used.

At a given temperature and pressure the course that a chemical reaction will take is determined (1) by the chemical affinity between the reacting substances and (2) by the relative masses of these substances. If the system consists of a solid immersed in a liquid, the rate of action depends on the amount of surface of the solid exposed to the liquid. If the product is an insoluble one and closely envelops the surface of the solid that is being acted upon, the rate of the action will be diminished because of diminution of the surface exposed. This effect of the accumulation of the insoluble product of the reaction increases, the longer the reaction goes on, and may finally practically check the process, which is clearly shown by the results of Lemoine cited above. While there can be no doubt of this effect, nevertheless, the differences in the rates of evolution of hydrogen during the times recorded above are in general too great to be accounted for solely on the basis of accumulation of the precipitate. Of this I became especially convinced by treating aqueous solutions with sodium amalgam; in these cases, where no precipitate forms, similar large differences in the rate of evolution of hydrogen occur.<sup>1</sup> Again it is well to

<sup>1</sup> This most interesting problem of the action of alkali metals and their amalgams upon aqueous solutions is being studied in this laboratory by Mr. Gustav Fernekas at present. His work is already well advanced.

bear in mind in this connection, that during the time of duration of the above experiments but small quantities of magnesium hydroxide or basic magnesium salts were formed; in fact, in many cases a precipitate was not at all discernible. I assured myself that from a bar of magnesium that had remained in a normal solution of sodium chloride long enough to be visibly covered with a white coating, hydrogen was nevertheless much more rapidly evolved than from a fresh bar of magnesium just placed in water.

One might further be inclined to ascribe the action of magnesium on these aqueous solutions to mere contact action, i. e., to so-called catalytic action of the solute or some of its ingredients. Tommasi<sup>1</sup> states that in the case of the potassium chloride solution we apparently have the best instance of such contact action, for here the potassium chloride remains unchanged and the magnesium hydroxide only is formed. Nevertheless even here it is not an easy matter to free the latter from "adhering chlorides" by washing. It would scarcely be helpful to dismiss the matter by saying that in these diverse solutions the rate of evolution of hydrogen is increased by the catalytic action of the solute when the hydrogen is liberated more rapidly than from water, and that the rate is diminished by the negative catalytic action of the solute, when the formation of hydrogen takes place less rapidly than from water.

All the facts above presented are very readily explained on the basis of the view of solutions which suggested this research; namely, that solutions are chemical combinations of solvent and solute according to variable proportions.<sup>2</sup> It is clear that if water is chemically bound to the substance dissolved in it, the readiness with which metallic magnesium or sodium amalgam will liberate hydrogen from different solutions will in general be different. Again, the difference of potential between magnesium and the solutions would be expected to be higher in the case of solutions that are vigorously attacked than in solutions in which the action is slight. The experimental data are in accord with this. If the chemical affinity existing between magnesium and the solution (regarded as a chemical combination of solvent with solute) is

<sup>1</sup> *Loc. cit.*

<sup>2</sup> The view that solutions are chemical combinations according to variable proportions, does not detract one particle from the law of definite proportions which is well established in the case of so very many compounds. Horstmann (*loc. cit.*) presents the whole matter so well that it is unnecessary to dwell further upon it here.

sufficient to overcome the cohesion of the magnesium, the latter is attacked; from the resulting compound hydrogen splits off, and the rest may all remain as a homogeneous liquid (*i. e.*, all may remain dissolved) or further decomposition into a precipitate, the hydroxide or basic salt, and a solution may occur and usually does occur after the action has progressed for a sufficient time. If no precipitate forms, the rate of change is not diminished by a decrease of the surface of metal exposed, and so the reaction is apparently aided. The more readily the dissolved products are removed from proximity of the surface of the metal by diffusion aided by mechanical stirring of some kind, the more rapidly the change progresses. Usually, as the gas is rapidly evolved, the liquid receives considerable stirring from this source. If the specific attraction called chemical affinity existing between magnesium and the solution is not sufficient at the temperature of experiment, to overcome the cohesion of the magnesium, no action will take place as in normal potassium hydroxide solution for instance; if the affinity is barely able to overcome the cohesion, the action will go on very slowly, as in the case of water. As stated above, magnesium amalgam does act on normal potassium hydroxide solution with vigor, liberating hydrogen, forming magnesium hydroxide and setting mercury free. The explanation of the action is similar to the one just given. Here the affinity between the solution and the amalgam is sufficient to disintegrate the latter, and magnesium hydroxide forms in spite of the fact that it is difficultly soluble. Under the conditions of the experiment, it is evidently easier to abstract magnesium from magnesium amalgam than to overcome the cohesion of pure magnesium. This is in harmony with the fact that magnesium amalgam does not form when magnesium and mercury are brought together at ordinary temperatures;<sup>1</sup> it requires a higher temperature in order that the union of the metals will take place.

The view that solutions are chemical combinations of solvent and solute may seem somewhat antiquated at the present time when purely physical conceptions of solutions are in predominance. But this older view is still held by eminent chemists and physicists, for it gives an adequate cause for the process of solution, for the thermal changes accompanying the latter, and for the

<sup>1</sup> At ordinary temperatures the affinity between these metals is not able to overcome their cohesions. Compare the work of Wanklyn and Chapman on magnesium amalgam in the *J. Chem. Soc.* [London], (2), 4, 141.

fact that (exclusive of the mass) the properties of a solution are never found to be quite equal to the sum of the properties of solvent and solute. Moreover, facts known at present concerning both dilute and concentrated solutions are entirely compatible with it, and it will no doubt prove a most valuable aid in further research.

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## THE VOLUMETRIC DETERMINATION OF MANGANESE IN IRON AND STEEL.

BY HARRY E. WALTERS.

Received January 26, 1903.

IN a recent number of this Journal, 24, 1206 (1902), there appeared an article by Stehman entitled "The Determination of Manganese in Iron and Steel" in which the author stated that in attempting to replace lead peroxide with ammonium persulphate and titrating with sodium arsenite, the silver salt, of course, caused trouble. If, however, the silver salt is thrown out of solution before the titration is begun, as insoluble silver chloride, the determination of the permanganic acid by a standard solution of sodium arsenite may be readily accomplished.

With the exception of the titration, the method is the same as that proposed by me in September, 1901.<sup>1</sup> While preparing that method the writer also tried to make a titration method but without success, as the hot solutions were titrated and the reaction between the excess of persulphate and the silver nitrate caused the results to be high and irregular.

Since the article by Stehman appeared, I have doubted the necessity of precipitating the silver as chloride, if the solution be cooled before the titration is begun. In order to prove the correctness of this view a number of samples were taken and treated as follows: 0.2 gram of the samples and a standard steel of known manganese content were weighed off into suitable test-tubes or beakers and 10 cc. of nitric acid (sp. gr. 1.20) were added to each. The solutions were heated until the samples were dissolved and all nitrous fumes driven off. Fifteen cc. of a solution of silver nitrate equal to 0.02 gram silver nitrate (1.33 grams of the salt to

<sup>1</sup> This Journal, 24, R. 12.



1 liter of water) were added to each. About 0.5 gram ammonium persulphate was added and the solutions were heated until the oxidation commenced, and then for about a half minute longer. The solutions were then cooled.

In preparing the iron samples 1 gram was dissolved in 30 cc. of nitric acid (sp. gr. 1.20) filtered into a 100 cc. calibrated flask and diluted to the mark. After thorough mixing, 20 cc. of the solution were transferred to test-tubes or beakers and a little ammonium persulphate added to destroy the combined carbon. Five cc. of a solution of silver nitrate (4 grams of the salt to 1 liter of water) and a little more persulphate were added and the procedure continued the same as for steels.

When the permanganic acid solutions were cold, they were treated as follows:

*First Series.*—The manganese was estimated colorimetrically.

*Second Series.*—The silver was precipitated as chloride and the solutions were then titrated with a sodium arsenite solution until the disappearance of the pink color.

*Third Series.*—The solutions were titrated with sodium arsenite without precipitating the silver as chloride.

*Fourth Series.*—The solutions were titrated with hydrogen peroxide without precipitating the silver as chloride.

The following results were obtained:

Sample.	Colorimetric.	Arsenite titration.		Hydrogen dioxide titration. Silver not precipitated.
		Silver precipitated.	Silver not precipitated.	
Steel No. 18 ..	0.28	0.269	0.281	0.27
" " 17 ..	0.47	0.46	0.48	0.47
" " 11 ..	0.53	0.55	0.544	0.533
" " 22 ..	0.57	0.588	0.593	0.59
" " 26 ..	0.40	0.44	0.428	0.426
" " 33 ..	0.49	0.495	0.493	0.492
" " 90 ..	0.90	0.92	0.902	0.89
" " 47 ..	0.43	...	0.43	0.43
Iron S.....	0.19	...	0.21	0.19
" No. 712....	0.22	...	0.22	0.21
" " 713....	0.23	...	0.234	0.24
" " 716....	0.24	...	0.24	0.245
" " 828....	0.16	...	0.16	0.15
" " 813....	0.13	...	0.11	0.11
" " 829....	0.18	...	0.17	0.19
Steel No. 68 ..	0.73	0.72	0.74	0.74

It will be observed that the results all agree closely whether the silver was separated or not, and that hydrogen peroxide (as was to be expected) may be used as well as the sodium arsenite. The end-point in all these titrations is not as sharp as might be desired but I think it is sharper if the silver is not precipitated. If the silver is not precipitated, the titration must be done quickly, as the persulphate and silver nitrate in solution react to reproduce the color, if allowed to stand.

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## THE CORROSION OF IRON.

BY W. R. WHITNEY.

Received January 30, 1903.

It is my object to add to the literature on this subject, the results of some observations of the action of water or steam under various conditions upon ordinary iron, coupled with some consideration of the principles involved.

Owing to the great use made of iron and steel, and the dependence placed upon them, it is not surprising to find that a great deal has been written upon the factors influencing their length of life when used for various purposes.

Practically the only factor which limits the life of the iron is oxidation, under which are included all the chemical processes whereby the iron is corroded, eaten away, or rusted. In undergoing this change, the iron always passes through or into a state of solution, and, as we have no evidence of iron going into aqueous solution except in the form of ions (probably electrically charged atoms), we have really to consider the effects of conditions upon the potential-difference between iron and its surroundings. The whole subject of corrosion of iron is therefore an electrochemical one, and the rate of corrosion is simply a function of electromotive force and resistance of circuit. If now we apply Nernst's conception of the source of electromotive force between a metal and a solution, we must conclude from the measured potential-difference that iron in contact with an aqueous solution tends to dissolve, ionize, or oxidize with a force expressed as equivalent to about 10,000 atmospheres' pressure at ordinary temperature.

In other words, iron should tend to dissolve in any aqueous

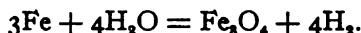
solution until the concentration of the electrically charged iron ions reaches such a concentration that the osmotic pressure is equal to the above value. This means that the saturated iron solution must be at least 450-fold normal, which is a concentration not practically obtainable. Thus far, the theory requires that iron should *tend* to oxidize in any aqueous solution. Whether it will do so or not depends on other conditions. Something may here be gained by a study of analogies. The dissolving zinc electrode of the Daniell or gravity battery, although possessing an enormous electrolytic solution-pressure, does not dissolve when the electric circuit is broken, but begins oxidizing immediately when connected through any external resistance to the copper pole. It is not enough then for oxidation or solution of the metal, that it have a *tendency* to dissolve; it must be in metallic connection with some other material capable of acting as an electrode, and this second electrode, if a positive element, must have a lower electrolytic solution pressure than the iron. Iron in contact with zinc and an aqueous solution will therefore not dissolve; but if copper replace the zinc, the iron will dissolve, the velocity of solution in these cases being determined by the resistance of the complete electric circuit. These two cases are often met with in practice. In marine boilers, zinc plates are sometimes suspended from the boiler tubes in the water, that they may be attacked instead of the iron. On the other hand, scrap iron is used very commonly to recover copper from solution in mine waters and other copper liquors, in which case the iron rapidly dissolves.

Hydrogen acts as a metal and is electrolytically classified in the group with copper when compared with iron and zinc. That is, if a cell were made up on the Daniell model, iron being used instead of zinc, and hydrogen in place of copper, the cell would generate a current when the iron and hydrogen electrodes were connected. Iron would then dissolve with a velocity dependent on the total resistance of the circuit. So also, and for the same reason, iron when placed in a solution containing hydrogen ions will dissolve as the hydrogen precipitates, just exactly as when placed in the copper salt solution. That iron does oxidize or dissolve in all solutions containing appreciable quantities of hydrogen ions is well known. This electrochemical relationship between iron and hydrogen is the primal cause of rusting.

This introduces at once an important point in connection with

the subject. Pure water is believed to contain hydrogen ions to the extent of approximately 1 gram for each 10,000,000 liters and should consequently act qualitatively like any other hydrogen-ion solution in oxidizing iron. It is to this extent an acid. It would evidently be quantitatively a very feeble solvent on this basis, if for no other reason than the high electrical resistance of the solution. This is simply another way of saying that in such a dilute solution the hydrogen ions can come into contact with the iron only exceedingly slowly, this contact being necessary for the action. Whether the iron on oxidation or on dissolving remains practically *in situ* as an insoluble compound, oxide, hydroxide, carbonate, basic salt, etc., or is removed as rapidly as it is oxidized, depends on the nature of the surrounding medium. If it be simply in vapor or in moist air, removal of the iron is out of the question. If it be in contact with aqueous solutions, the removal of the iron will be determined by the nature of the negative ions in the solution. If insoluble compounds can form at the point of corrosion, the iron will not be removed. This is illustrated by the common precipitation of oxide or rusting due to the oxygen dissolved in the water; if no such insoluble compounds are formed, the iron will be eaten away, the surface remaining bright. Both of these processes are very common in practical experience.

There is no doubt that iron, even at ordinary temperatures, reacts with pure water, in accord with this conception. The experiments on this point, carried out by Deville<sup>1</sup> at high temperatures only, showed a balanced condition at various temperatures for the reaction



He found experimentally that water vapor in contact with iron must produce a certain concentration of hydrogen gas to be in equilibrium; in other words, if the hydrogen was continually removed, the iron could continually oxidize. Within the range of temperature employed (200° to 1000° C.), he found that the pressure of the hydrogen produced by the action between iron and water increased as the pressure of the water vapor was increased. As the temperature rose, the hydrogen concentration (or pressure) at equilibrium diminished; in other words, the lower the temperature in his experiments, the greater the tendency for oxidation of

<sup>1</sup> *Ann. Chem. (Liebig)*, 157, 76 (1870).

the iron. According to these results, we should expect water to act on iron to generate hydrogen even at ordinary temperatures, and it is a well-known fact that very finely divided iron such as is obtained by dry reduction of iron salts, reacts with pure water and generates hydrogen.

This fact, that pure water causes solution of iron, is in accord with other experimentally discovered facts. Mr. G. O. Adams, in connection with a thesis presented to this institute in 1900, made analyses of various samples of gases collected from radiators in different houses where the hot-water gravity heating system is used, and where different water supplies are concerned, and always found a large quantity of hydrogen gas. In most cases, on opening the air-cock of the radiators the gas could be lighted with a match. A number of such mixtures were analyzed. These varied in composition, but were mainly mixtures of nitrogen and hydrogen with usually no oxygen. The hydrogen-content varied from 44 to 78 per cent. by volume. Measurable quantities of carbon dioxide or of hydrocarbons were not usually present.

It is very generally accepted by authorities on the corrosion of iron that the presence of carbonic acid is necessary; but, as water itself must be considered as not greatly different in hydrogen-ion-concentration from a carbonic acid solution in contact with air, it seems *a priori* probable that this accepted idea is incorrect.

Assuming the laws of Henry and Dalton to apply to the solubility of carbonic acid gas in water, also that the solubility of the pure gas under ordinary pressure is one volume for one volume of water (which is correct at 15° C.) and, finally that the normal content of carbonic acid in the atmosphere is 2 parts in 10,000 by volume, we should expect water in equilibrium with air containing this concentration of carbonic acid to contain 0.0002 volume carbon dioxide per volume of water. This corresponds to a concentration of the carbonic acid equal to 0.00001 mol per liter or 0.00002 normal. From the dissociation constant  $(3040 \times 10)^{-10}$  determined by Walker,<sup>1</sup> and to which my attention was called by Professor Noyes, it follows that the first hydrogen of the acid is 16 per cent. dissociated at this concentration. From this it follows that 10,000,000 liters of water containing carbonic acid in equilibrium with ordinary air at 15° contains 16 grams of hydrogen ions, or only 16 times as many as perfectly pure water con-

<sup>1</sup> *Ztschr. phys. Chem.*, 32, 137.

tains. At the boiling temperature the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than that in pure water, for not only is the solubility of the gas greatly diminished, but the dissociation of water is greatly increased by rise of temperature. Moreover, the distilling water would rapidly reduce the concentration of any carbonic acid capable of dissolving in water at 100° C.

The following experiment bearing upon this point is one which may have been frequently tried by others, but is worthy of note. To learn whether carbonic acid was necessary to iron-rusting, a clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper, was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80° C., and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass, that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide.

Mr. J. A. Collins, in connection with his thesis of 1898, performed a similar experiment which shows that the iron is dissolved in the water and that its appearance as rust is a secondary phenomenon due to the action of oxygen on the solution. A cleaned iron pipe 0.5 inch by 15 inches, sealed at one end and

having a screw cap to fit the other, was filled with boiling distilled water, and the boiling continued by heating the pipe until half the water had boiled away. While still rapidly distilling, the cap was screwed on tightly and the tube heated to about  $125^{\circ}\text{C}$ . for an hour. On cooling and removing the water from the pipe, it was found to be perfectly clear and colorless, but, on exposure to air in a glass vessel, it rapidly precipitated rust. The pure water had dissolved iron in some form from the clean metallic surface, and this had remained in solution until precipitated by the oxygen of the air. In experiments with air-free water in contact with iron, in glass bottles and flasks, Mr. Collins let into the flasks containing only the pure water together with its vapor and the bright iron, air which had been freed from carbonic acid by being exposed to the action of a barium hydroxide solution in a closed bottle for twelve hours, the bottle being repeatedly shaken to hasten the absorption. In case of this treated air, the production of rust in the flasks was evidently as rapid as with ordinary air.

A similar experiment with purified oxygen gave the same result. One is forced to conclude from such results that if the rusting is due in any way to carbonic acid it is rapidly brought about by such a quantity of this gas as is left in air or oxygen after treatment with a barium hydroxide solution; in other words, by an inappreciably small quantity. As this acid could owe its activity solely to its hydrogen ions, because of the fact that the carbonate ion has no rusting or dissolving action on the iron, it is interesting to note that in the case of recently boiled water, the hydrogen-ion content due to carbonic acid may well be as low as the hydrogen ion content due to the dissociation of pure water.

Iron dissolves in pure water qualitatively just as in a solution of copper sulphate, hydrogen being deposited in place of copper. The velocity with which this process proceeds will depend on the temperature and on the hydrogen-ion-concentration in the water. When this concentration is so great that the potential-difference exceeds a certain value, the hydrogen will be evolved as gas, separating from the liquid at the surface of the iron as bubbles. This potential value depends on the state of the surface, so that it is usually higher than the theoretical value for polarization by hydrogen where the gas is in equilibrium with the solution. Below this value, the hydrogen, which is nevertheless being deposited upon the iron, but at a concentration below that corresponding to

atmospheric pressure, slowly dissolves in the water, forming an ordinary solution of it, and escapes by diffusion. Its solubility will presumably be proportional to its pressure even though this is below atmospheric pressure.

It was shown by Faraday that an electromotive force below that necessary for visible electrolysis of a solution, was still capable of producing a continuous though feeble current which was then attributed to metallic conduction of the solution. Helmholtz, by his studies of polarization, showed this to be due to actual electrolysis proceeding as above stated. This polarization phenomenon should greatly limit the velocity of solution of the iron, even if no other complicating effect due to the production of an insoluble compound, an oxide or hydroxide, in case air be present. This is usually the case in practice. The production of a compact adherent coating of oxide on the surface of the iron generally retards the corrosive action. Especially is this true at temperatures of steam where the magnetic oxide is formed. This oxide always forms as an adherent solid coating on the iron and seems to be interrupted only by cracks caused by its unequal coefficient of expansion compared with the iron. The red oxide or rust is always flocculent and spongy and, besides not protecting the iron, actually seems to increase the velocity of corrosion in its vicinity. It is common to attribute to the red oxide or rust a catalyzing effect on the corrosion of iron.

If the primary rate of corrosion of iron independent of subsequent formation of insoluble substances is simply dependent upon the concentration of the hydrogen ions of the water, anything which reduced this concentration should also reduce the corrosion. The principles of equilibrium of chemical reactions when applied to the dissociation reaction of water should show how, practically, to accomplish this reduction. In this case the product of the concentration of the hydrogen and hydroxyl ions must remain constant in any aqueous solution, for the principle involved declares this product to bear a constant relation to the concentration of undissociated water molecules and this is itself evidently constant in aqueous solutions. From various measurements we are led to believe that the product of the concentrations of the hydrogen and hydroxyl ions is approximately  $10^{-14}$ . In pure water the concentration of each of the two water ions, hydrogen and hydroxyl, is therefore evidently  $10^{-7}$ . If additional hydroxyl ions



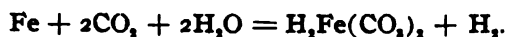
are added to the water in any way, the concentration of the hydrogen ions must correspondingly diminish, so that the product may remain constant. Thus the corroding power of the water, if due to the hydrogen ions, would be reduced. This reduction of the hydrogen ion concentration may be brought about by the addition of any alkali to the water. That the corrosion is thereby diminished is a well-known fact and one that already receives many practical applications. Iron and steel tools in process of manufacture, between the roughly ground state and the final polished condition, are often kept under water saturated with lime. This prevents the rusting which would quickly take place if they were left in moist air. The effect of the lime must be attributed solely to the hydroxyl ions which in turn reduce the concentration of the hydrogen ions of the water. Neutral salts of calcium do not exert this effect and hence it can not be attributed to the calcium compound nor to the calcium ion. Other soluble alkalies do it equally well and these contain, in common, only the hydroxyl ion.

One of the most common components of the many boiler-compounds which are used to prevent pitting and corrosion in boilers, where the water used is very pure and consequently does not form a protecting layer of scale upon the iron, is some form of alkali. The alkalies usually used are caustic, slaked lime, carbonates, borates, aluminates, etc., which are in every case compounds readily undergoing either dissociation or hydrolysis and producing hydroxyl ions thereby. Thus again the concentration of the hydrogen ions is reduced. Conversely, the concentration of hydrogen ions would be increased by the addition of any salt whose hydrolysis would produce hydrogen ions, and for this reason magnesium chloride, ammonium chloride, and similar compounds may increase the corrosive effect of waters containing them.

Free alkali added to a boiler water not only greatly reduces the concentration of the hydrogen ions, from whatever source, thus diminishing the electrochemical reaction of interchange between hydrogen and iron in the boiler itself, but also produces another valuable effect. If a steam or hot-water heating system is fed with a water which is not naturally alkaline, a part at least of the carbonic acid, which it always contains, will be driven from the water on boiling and pass to the cooler portion of the system to be redissolved in condensing water. Thus the return pipes of the

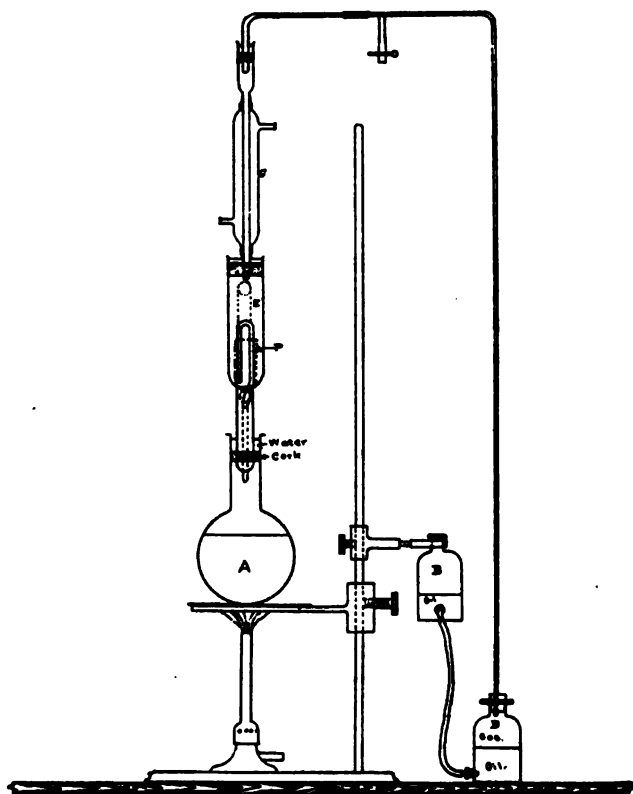
system will be subjected to the action of this acid or hydrogen-ion solution. No protecting scale of salts from the water being produced in these return pipes, such as is almost always produced in the boiler itself, the corrosive action will be most marked in the return pipes, and especially where the pipes are exposed to the action of continuous supplies of the water in motion. This will prevent the establishment of equilibria and the iron will be continually removed. It ought also to be removed according to the previous discussion, though more slowly, even if no carbonic acid or other acid were present, because of the hydrogen ions of the pure water. This reaction could again be reduced by the presence of volatile alkali in the condensed water, but in practice this latter is usually a negligible effect compared with the effect of volatile acid.

I wish now to show that the effect of the carbonic acid is actually a cyclic one, the same molecule of acid doing unlimited corrosive work, and that the very harmful corrosion of return pipes in many heating systems may be directly attributed to this usually inconsiderable and unnoticed ingredient of the water. To make this point clear, let us imagine a steam-heating system made up of a boiler, with steam pipes leading to various heating stacks and radiators from which return pipes bring the condensed steam back to the boiler below the water-level. For simplicity, we assume that the plant is run without the addition of water after the boiler has been originally charged. In other words, no steam is blown out into the air and the plant is not used, as some are, to incidentally supply hot water for foreign uses, which thus requires a continual water feed. Our closed system usually contains, when in actual running condition, a number of dead-ends where gases have accumulated and where the pipes are cold. This may be observed in many radiators of common type. Into this colder portion of the system, the gases such as oxygen, nitrogen and carbonic acid, which were originally in the feed water, will collect. Here they will dissolve in the condensed water which is to return to the boiler, the carbonic acid being especially soluble. The carbonic acid or its active hydrogen will cause the solution of iron from the return pipes and this iron will be carried back towards the boiler as bicarbonate of iron, being held in solution just as is calcium carbonate in water containing carbonic acid. This may be represented by the reaction



In the case of the bicarbonate of calcium solution, it is well known that boiling it decomposes the salt and liberates half of the carbonic acid, leaving a precipitate of calcium carbonate. In case of the soluble bicarbonate of iron, as will be shown later, the decomposition of the compound by heat, liberates all of the carbonic acid instead of half of it and produces the insoluble oxide or hydroxide of iron. Whether this decomposition of the soluble iron salt takes place in the boiler after the solution has returned to it, or in the return pipe where the proximity to the boiler produces a sufficiently high temperature, is of no immediate importance. In either case, the carbonic acid is all set free and must immediately return with steam to the cooler parts of the system; there again it will dissolve in the condensate, again render soluble some iron and carry it towards the boiler and so forth. In each cycle of this kind hydrogen will be set free which will remain in the cooler parts of the system, as it is but slightly soluble in water. It seems necessary, therefore, that in common practice a very small quantity of carbonic acid must often cause an unlimited amount of corrosion, without in any way losing its power to continue the process. The process of corrosion of the iron in this case will amount *in toto* to the union of iron with the oxygen of water and liberation of hydrogen, the carbonic acid acting merely as a catalyzer, where the mechanics of its action is apparent. This peculiar condition of affairs has been observed by us in certain large heating systems where we have found, first the carbonic acid of the feed water; secondly, much carbonic acid mixed with hydrogen, nitrogen, and oxygen in dead-ends or cold parts of the system; thirdly, water in the return pipes, where very rapid corrosion of the piping was taking place, in which much dissolved bicarbonate of iron was found; and, finally, much precipitated oxide of iron in the boiler and hottest parts of the return pipes.

It has been possible also to reproduce these phenomena in the laboratory in various ways and in some cases in glass apparatus where the complete cycle becomes practically visible. In connection with his thesis, Mr. C. L. Wright arranged an apparatus of which a sketch is shown. Pure distilled water was boiled in the flask A, and various quantities of air and carbonic acid mixtures were enclosed in the system which was kept nearly at atmospheric



pressure by the liquid seal made by the bottles B connected with the condenser C. The steam condensed and took up a little of the carbonic acid; this solution came into contact with a piece of cleaned iron pipe, P, from which the outer layer had been removed in the lathe. This iron was supported in an extractor, E, between the condenser and the boiler in such a way that it was alternately covered with the water and uncovered by the intermittent siphon action of the extractor.

In the first few experiments a precipitate was soon formed in the boiler which was not analyzed, but which was evidently a mixture of hydroxide of iron and silica from the glass. Subsequent experiments in the same apparatus differed in result from the first one and showed that, in the absence of free oxygen, the boiler water simply became black and opaque but showed little or no

precipitate. The glass tube leading from the condenser to the boiler was also quickly coated with a black deposit of iron oxide. It was evident that iron was being dissolved and the resulting compound decomposed in the boiler, and in the hot return tube, but it was at first thought peculiar that the precipitate which appears when the glass or flask is a new one, was not produced in subsequent experiments with the same apparatus. This led to attributing the actual formation of a precipitate in the first case to the presence of dissolved glass. The dark color could only be due to the iron. The clear, black, filterable solution obtained from such previously used apparatus was then shown to be a colloidal solution of iron oxide by the following method: Small quantities of such salts as sodium and barium chloride were added to portions of the clear, black water, and they caused an immediate coagulation and a consequent heavy precipitate, coupled with complete decolorization of the solution. This precipitate, well washed by decantation with pure water, was treated with dilute sulphuric acid in a closed vessel and pure air passed through this and then through a vessel containing a barium hydroxide solution. The failure to produce a precipitate of barium carbonate in this barium hydroxide solution showed that the original compound did not contain a carbonate. The precipitate was shown to contain iron by dissolving it in acid, oxidizing and precipitating the ferric hydroxide by ammonia. The formation of this colloidal solution of ferrous oxide is in exact accord with the principles which determine the formation of colloidal solutions in general. It is a general principle that whenever any substance which is by nature insoluble, is formed in water, it will tend to remain in a colloidal or suspended state until coagulated by electrolytes.

In the production of most precipitates in common laboratory reactions, there are always sufficient electrolytes present to account for the coagulation of the insoluble substances, if we may judge by the concentration usually necessary where measurements have been made. Where this is not the case, a colloidal state usually results. In the case at hand, there are practically no electrolytes present when the soluble ferrous bicarbonate is decomposed by heat, as this process requires the presence of but exceedingly small quantities of soluble salts in the solution at any one time. The insoluble ferrous oxide consequently remains in the colloidal state. This colloid may be precipitated by salts dissolved from

the glass vessel, if of sufficient concentration, as was the case with new glass apparatus, and in this respect this colloid is like many others, such as platinum and silica.

The ease with which the soluble iron salt is decomposed by heat was well shown in the glass tube connecting the condenser and boiler, the return pipe of the above experiment. Above the stopper of the flask, where this tube was fairly cool, the glass remained clear, but below the stopper where the tube was heated by the steam of the flask, it was covered deeply with a black deposit, probably ferrous oxide. The deposition of this substance at this part of the return tube, commenced almost immediately on starting the experiment.

An experiment carried out in this way where pure water and carbon dioxide were used, where analysis showed the gaseous mixture to contain 11 per cent. carbon dioxide, produced such rapid corrosion of the iron that within a few days nearly a third of the exposed surface had been eaten away to depths of several hundredths of an inch, at which rate an ordinary pipe would not last more than a few months. It is not surprising that carbonic acid should dissolve iron under these conditions, but the fact that this corrosive action is a cyclic one, in which under suitable circumstances even a trace of carbonic acid may dissolve an unlimited quantity of iron without losing its corrosive power, has not received sufficient attention.

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## A PROPOSED METHOD OF TESTING WOOD TREATED TO RESIST FIRE.

BY CHAS. F. MCKENNA.

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In the spring of 1902 an effort was made by the Bureau of Buildings of the Borough of Manhattan, New York City, to secure more certitude as to the qualities of the so-called fireproof wood which was being delivered in the city for use in high buildings.

Methods of test which have been in vogue for some time in the Bureau of Buildings were stated to be inadequate for the proper discrimination between well-treated wood and that which was

treated only imperfectly and was presumably at times not fireproof in any sense. These methods included the test, long in use in the Navy Department, of exposing shavings to the influence of heat while they rested upon a wire screen, timing the rate of combustion, as well as estimating its extent; also the splinter test as practiced in the simple expedient of holding a splinter of wood in and across the flame of a Bunsen burner or upon a red-hot iron plate; also, what may be called the cob-work test, by which prisms of wood about 6 inches long and 1 inch, more or less, square, are piled with air-spaces between them and exposed to the flame of a Bunsen burner. There was finally the more meritorious test of Professor Woolson, of Columbia University, which he calls the timber test, in which specimens of wood 1 inch square and 1 foot long are laid in pairs across the top of a 6-inch gas furnace and exposed to a presumably constant temperature of 1700° F. The depth to which the specimens were charred was subsequently measured and the unburned area used as a basis of comparison.

The fundamental fault with all of these methods of test lies in their neglect of the chemical factors involved in the decomposition of wood under the influence of heat. Nor were proper attempts made to standardize the conditions governing the application of the flame, the access of the air, and the surrounding temperatures, etc. Again, no instrumental means of registering the differences in the results obtained were suggested. In the timber test, the accurate measure of the unburned area does not answer this need, and fails of its purpose where the conditions during the test have so varied.

In the course of the discussion upon this subject which took place about the time mentioned in New York City, there was found to be a demand for an "inspector's test"; that is, for an instrumental and simple test giving results measurable and free from guess and which could be carried on at the place of delivery of the timber. The writer approached this subject from the chemist's side, and his first effort was to undertake distillation tests in closed retorts.

Inasmuch as it was early admitted that these fire-proofing processes could not prevent the destruction of wood by fire operating under its worst aspects but could only stay the disintegrating effects long enough to present the hope of gaining some advantage over the demon, it seems strange that the search for

this test did not then take the form of a study of the reactions proceeding during the inflammation and combustion of the wood, as well as of those accompanying its destructive distillation for the purpose of finding facts leading to more certain means of measuring the retarding values of the various treatments to which wood is subjected for this purpose. The writer outlined such a study by means of destructive distillation of samples of natural and of treated woods; for, although combustion and inflammation with free access of air are undoubtedly the most common conditions of a conflagration, yet the breaking down of the cellulose molecule, of the fundamental tissues of the wood, as well as of its allied organic and mineral constituents, takes place from the center of large masses as a distillation without air, just as it does also when timber and planking burn at the back of a hot brick wall, or within a metal-cased door or window frame, or where electric wiring passes over wood encased in concrete flooring or in walls. The prosecution of such studies has been stayed through lack of means, but the initial efforts nevertheless have resulted in this proposed method of testing which, with the apparatus offered, seems to be the means for easily making an extended series of critical observations.

Some early distillations made upon charges of wood shavings in 6-ounce glass retorts heated by a triple Bunsen burner developed the fact that when the temperature reaches  $250^{\circ}$  C. the volatile products cease to be driven off and temporarily a vacuum is produced if the heat is not promptly raised. This took place in every case in not over three minutes of such heat conditions, and also, under the same conditions, the yield of gas was quite uniform for different woods. To secure higher temperatures in a brief time, the electric wire method was adopted. This led to the invention of an electric test retort, and this in turn, when tried on numerous lots of wood, quickly developed the fact that the little instrument was exactly adapted to meet all the requirements of an inspector's test when the original untreated wood is at hand to compare with the treated, and perhaps also where original samples cannot be obtained. This apparatus is described in my paper presented at this meeting under the title "Electric Test Retort."

In using it for the study of fire-proof wood, it has been my aim to simplify it, as well as the details of the testing, in order that



numerous samples of wood could be examined easily and quickly.

A large gas burette was provided, having with it a large reservoir for leveling, and this in connection with the electric test retort were all that I found necessary for making critical tests of treated woods. Absorption tubes for the pyroligneous products could be provided, but in the work in hand the necessity was obviated as much as possible by the high initial heat and by providing that the water in the gas burette shall absorb the pyroligneous products until nearly saturated with them.

Violette, as quoted by Sadtler<sup>1</sup> in studies devoted to distillation of wood, found that when it is *slowly heated* the water and pyroligneous acids, alcohols, and creosote are all driven off up to and at 280° C. to the extent of 63.8 per cent. of the original weight; a large volume of gas up to and at 350° C.; and up to and at 430° C. a total loss of weight of 81 per cent. is experienced. But *quickly heated* wood placed at once in the retort at 432° C. lost 91 per cent. Senff,<sup>2</sup> in distilling a variety of woods in 100 kg. charges, found that the uncondensed gases in slowly heated samples varied from 17.17 per cent. to 29.23 per cent. with an average of 22.64 per cent. for fifteen examples of different woods; the uncondensed gases resulting from quickly heated samples varied from 24.07 per cent. to 35.56 per cent., with an average for fifteen samples of 31.50 per cent. He found that the charcoal varied from 23.23 per cent. to 34.68 per cent, with an average of 27.59 per cent. in slowly heated samples, and from 20.20 per cent. to 31.59 per cent., with an average of 23.09 per cent., in quickly heated samples. He also found the very important fact that the more common woods, as oak, beech, birch, poplar, and pine, show by the results of the destructive distillation that they resemble one another very much in fundamental composition and give like results in the yield of the respective products.

Hence, we should have in the electric test retort an opportunity to heat quickly to the highest temperature, thus obtaining the maximum gas yield. Fortunately, also, in this test retort, it is not strictly a distillation without access of air; it is really, in a small way, quite a perfect duplication of conditions existing at the beginning of a fire in a closed space, and we have also in this apparatus an opportunity to introduce air in measured quantities, if required.

<sup>1</sup> "Handbook of Industrial Organic Chemistry," second edition, p. 344.

<sup>2</sup> *Ber. d. chem. Ges.*, 18, 60.

In conducting the test, a small charge of wood, cut as a little cylinder about 0.5 inch long and 0.25 inch wide, weighing about 500 mg., is placed within the platinum wire basket, the dome is placed upon the apparatus and clamped tightly by suitable means, and the tube leading off from the dome is connected to the gas measuring burette having the usual reservoir tube attached. A current at a difference of potential of 120 volts and a strength of from 7 to 12 amperes is used. Great precautions are needed to keep the current strength steady, and a 7.5 ampere current is the best strength for this experiment. Tests made with the Le Chatelier pyrometer show that the temperature within the coil with a 7.5 ampere current is  $680^{\circ}\text{C}.$ ; with a 10 ampere current the temperature rises at the end of three minutes to  $840^{\circ}\text{C}.$  The charge of wood is subjected to the effects of a current of 7.5 amperes for exactly two minutes, the gas being conducted to the burette. Observations of the glow, if any, and of the amount of smoke and the character of same, can all be made and recorded. At the close of the two-minute interval, the current is shut off, the gas burette stop-cock closed and air admitted to the retort by opening the tubulure at the side. The gas in the burette is cooled, and the volume measured. Or, if a series of tests are being made, the conditions of which are known and invariable, the volume could be read without correction, where so noted. So also, the correction for the volume of air increased by the heat of the contents of the retort can be neglected, for it will be found to be a very constant figure under uniform conditions. Thus, with some experiments in blanks, in heating without the charge with a 7 ampere current for two minutes the results were 23.6, 22.8, 22.8, 22.6, and 22.6 cc. With a 6.5 ampere current for two minutes, the results were 21.6, 21.6, and 21.6 cc. Other experiments gave, with a 7 ampere current for two minutes, 21 cc. average; with a 7.5 ampere current for two minutes, 24 cc. average; with an 8 ampere current for two minutes, 26.5 cc. average; and others with an 8 ampere current for two minutes, 26 cc. average.

The following experiments demonstrate that the gas yield and coal from the distillation of small pieces of some of the more common woods could be used as a criterion of the extent of retardation of fire caused by the proofing processes.

Spruce; 0.500 gram; fireproof; heated for two minutes by 9 ampere current:

	cc.
Gas yield.....	116.5
" " .....	124.5
" " .....	117.0
Average .....	119.3

The same wood leached in boiling water and dried to normal moisture:

	cc.
Gas yield.....	136.5
" " .....	129.0
" " .....	136.0
Average .....	133.8

Birch; 0.500 gram; 8 ampere current for two minutes:

Gas yield.	
Untreated. cc.	Treated. cc.
164	151
165	160
171	162
165	153
167	...
Average, 166.4	Average, 156.5

The four specimens of char of the treated wood showed an average weight of 147.6 mg., and those of the untreated wood averaged 100 mg. The percentage of charcoal left in the treated wood was 29.5 per cent., and in the other 20 per cent.

With exercise of more care, similar experiments gave the following results:

Birch; 0.500 gram; 7 ampere current, 125 volts, two minutes:

Gas yield.	
Untreated. cc.	Treated. cc.
125	95
127	105
124	105
126	103
126	108
132	104
Average, 126.6	Average, 103.3

Charcoal.			
Untreated.		Treated.	
Gr.		Gr.	
0.1037		0.1643	
0.1026		0.1540	
0.1065		0.1595	
0.1025		0.1700	
0.1062		0.1681	
0.1016		0.1661	
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Average,	0.03541	Average,	0.16366

The following experiment was performed with the assistance of one of the companies practicing the fire-proofing art: A sample of birch, of which I was given an initial untreated specimen, was fireproofed for me in a small test cylinder, using a solution of the density with which they were accustomed to operate on a large scale. Two solutions of less density by one-third and two-thirds of the dissolved salts were also prepared and used on specimens of the same wood on separate runs of the cylinder. I was thus provided with four specimens of wood of the same lot: the first, natural; the second, treated with a dilute solution; the third, with one more dense; and the fourth, with one most dense. These were numbered "0," "1," "2," and "3," respectively. In the test retort they gave the following results:

0.500 gram; 7 ampere current, 125 volts, two minutes:

Gas yield.			
"0"	"1"	"2"	"3"
cc.	cc.	cc.	cc.
112	89	99	97
108	92	97	95
104	88	92	92
107	87	99	93
107	89	95	91
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Average,	107.6	88.6	96.4
			93.6

Average weight of the charcoal from each:

	Milligrams.	Per cent.
"0".....	103	20.6
"1".....	136	27.2
"2".....	120	24.0
"3".....	133	26.6

If the decomposition into gaseous products and coal measures the value of the treatment, the least dense solution gave the best result, which is probably true, as it was an alum process, and the

penetration of the cell-walls was probably more perfect with the most dilute solution.

*Experiments with Yellow Pine*, treated by another process and patent than the preceding. This yellow pine gave the following results (as there was no original stock offered, the "untreated" specimens were obtained from scraps of yellow pine in a carpenter shop) :

0.500 gram ; 8 ampere current, 125 volts, two minutes :

Gas yield.	
Untreated. cc.	Treated. cc.
125	87
131	86
128	88
133	86
134	86
Average, 130.2	86.6

Average weight of four samples of charcoal :

Untreated.	Treated.
0.0979 gram or 19.58 per cent.	0.1912 gram or 38.24 per cent.

Yellow pine untreated :

(a) Dried.

(b) With normal moisture, 7.1 per cent. more water than (a).

Gas yield.	
(a) cc.	(b) cc.
139	128
136	132
143	134
Average, 136	131

Charcoal, average weight :

(a) Gram.	(b) Gram.
0.102	0.0963

Yellow pine, treated :

(c) Dried.

(d) With normal moisture, 3.6 per cent. more water than (c).

Gas yield.	
(c) cc.	(d) cc.
90	92
91	88
89	88
90	85
Average, 90	88

Charcoal, average weight:

(c)  
Gram.  
0.198

(d)  
Gram.  
0.1882

Three questions arise: Will not errors be introduced by the moisture of the wood? This is to be met in the same way as in previous methods of test; namely, by the preparation of dried samples subsequently exposed for the absorption of the normal amount of water. Whether it would vitiate the results obtained by inspectors having limited facilities for such work, will have to be determined. Are not the results modified by the superior density of the treated sample over the normal wood that contains no salts? Naturally this should be so in finding the weight of the char residue; but in all experiments it seems to be an unimportant quantity, and in some it would appear that the wood which is heavier from treatment with the dense solution of an inferior fire-proofing salt will give a very large gas yield. Would not gases generated from the chemicals also modify the results? The only process where it possibly would, is in using ammonium salts or carbonates and proper provision should be made for the absorption of the gases as each case would require.

It would seem to me to be indicated by the preceding that the degree to which total decomposition without air can be inhibited by previous chemical treatment in wood subjected to a high heat can be definitely measured by subjecting small test pieces to distillation, that this test operation can be easily, quickly, and accurately performed in the small retort as shown, and that the number of such tests which can be made in a short time on small pieces is so great that a good average could be selected in chips from different parts, interior, exterior, etc., of lots of timber as delivered. It seems probable also that in the conditions surrounding experiments in such a retort, an equally accurate measure can be found of the resistance to inflammation of woods before and after treatment, with access of air.

I hope to continue such experiments in the future, if circumstances favor.







## AN ELECTRIC TEST RETORT.<sup>1</sup>

BY CHAS. F. MCKENNA.

Received January 29, 1903.

THE apparatus described in this paper is the result of demands made to carry on distillations of many samples of wood in small pieces. After its development was reached, it appeared also to afford so many opportunities for use in the laboratory in situations where the crucible is used, and even for the combustion of carbon, the ignition of minerals, etc., that I have thought it worthy of description here.

It consists of a vessel of Jena glass about 4 cm. in diameter, with a dome-shaped piece attached to it by clamps and from which a tube leads to a proper absorption apparatus. The upper edge of this glass vessel is turned flat and ground to a perfect matt and plane surface. The dome is provided to match this and fit with a similar flat surface. A simple form of clamp may be used to hold the dome upon the retort. At present I am using a small and not elegant, but very satisfactory, wood clip such as is used in holding photographic papers. With a very slight lubrication of the ground glass surfaces and two of these clips, a higher pressure can be resisted than is likely to be met with in using gas burettes and reservoirs. The globe of this glass apparatus terminates below in a tube about 1.5 cm. in diameter cemented into a wood base, up through which go two leading-in wires of copper. In the terminals of these are fastened the terminals of a platinum wire which is wound to make a basket-like coil, and this forms the retort proper in the center of the glass globe. In the side of the large glass tube is a smaller one provided with a stop-cock to admit air, oxygen, etc.

In operating with this apparatus, the connections are duly made with a lighting circuit, and the current regulated by a metal or water rheostat, or perhaps by both, if convenient. For the work and the purposes for which this instrument has so far been used, I have made some temperature observations by means of the Le Chatelier pyrometer. The current was left as closely as possible at 7.5 amperes, with a difference of potential of 120 volts. The temperature within the coil, when protected from cooling by air, was found to be 680° C. Using a 10 ampere current, the temperature

<sup>1</sup> Read at the Washington meeting of the American Chemical Society.

rises at the end of three minutes to  $840^{\circ}\text{C}$ . Of course it is possible to reach temperatures of any degree up to the fusion of the wire.

I have found this, as already stated, to be extremely useful in conducting several distillation tests with small charges of wood. It could be adapted for use as an ignition crucible by replacing the semi-spherical coil with wire wound as a cone and preparing cone-shaped asbestos pads to fit in the same. It would then be possible to use the apparatus for igniting limestones, cements, etc. It could, I believe, be equally as well adapted for the combustion of carbon from steel, since the carbon residue could be filtered upon an asbestos cone pad and placed in this coil, and by preparing the proper train of apparatus, a perfect combustion could be made. Its size and convenience and adaptability seem to me to promise much in this and similar uses.

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### THE DETERMINATION OF POTASH IN FERTILIZERS BY SUBSTITUTING MILK OF LIME FOR AMMONIA AND AMMONIUM OXALATE AS THE PRECIPITANT.

BY C. L. HARE.

Received January 9, 1903.

THE Lindo-Gladding method for the determination of potash in fertilizers possesses one particularly objectionable feature. The evaporation and ignition of an aliquot portion with sulphuric acid for the purpose of expelling ammonium salts and destroying dissolved organic matter is a tedious process and involves loss from spattering during evaporation.

A reliable modification which would exclude this feature would be highly desirable. At the sixteenth annual meeting of the Association of Official Agricultural Chemists, Ross presented a method based upon the use of barium carbonate as a precipitant for phosphates, iron, alumina, etc. He later suggested milk of lime as a precipitant and the writer in 1901 reported results obtained by collaborators on official methods for potash determinations.

The method employed is as follows: Weigh out 10 grams of the sample and boil with about 350 cc. of water for thirty minutes; while hot, add milk of lime till slightly alkaline. Cool, make up

to 500 cc. with water and remove 50 cc., corresponding to 1 gram. Acidify with hydrochloric acid, add platinum solution and evaporate to soft dryness over the water-bath. The residue is then washed with 80 per cent. alcohol and ammonium chloride wash as in the Lindo-Gladding method.

In case of fertilizers containing organic matter, treat 10 grams of the sample with dilute sulphuric acid (1:1) and incinerate; moisten the ignited mass with dilute sulphuric acid (1:1) and heat to aid in removing from the dish, boil with 350 cc. water and proceed as before. The milk of lime precipitates all lime except that present as sulphate and the solubility of the sulphate being only 1 in 500, the aliquot of 50 cc. will contain only 0.1 gram of that substance, an amount readily removed by the ammonium chloride wash-water and insufficient to cause material trouble either when the solution is made with water direct or after incineration with sulphuric acid. The potassium platonic chloride crystallizes well, and, after washing with alcohol, the salts of lime appear in light flakes which never require more than six washings with ammonium chloride wash for complete removal.

The modification possesses several advantages over the Lindo-Gladding method: First, the precipitation of lime is immediate and there is no delay at this point; second, evaporation to expel ammonium salts is eliminated; third, probable loss of potash during the evaporation is obviated; Fourth, washing the potassium platonic chloride with alcohol and ammonium chloride wash may be performed thoroughly with greater ease and rapidity, while no larger amount of platinum is required than by the Lindo-Gladding method. The accuracy of the method is evidenced by results as shown in the tables. It has been used by the writer upon several hundred samples of miscellaneous fertilizers as a check against the Lindo-Gladding method, but it is evident that the modification would not be applicable to fertilizers containing ammonium salts.

Table I gives parallel results by the milk of lime and the Lindo-Gladding methods upon fertilizers containing no organic materials, the solution in each case being made by boiling the sample with water.

TABLE I.

Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.
1.02	1.29	1.42	1.62	4.51	4.53
2.33	2.20	1.91	1.91	1.97	1.87
2.42	2.42	1.95	2.12	2.54	2.64
2.56	2.45	2.44	2.36	1.09	1.04
1.10	0.90	2.14	1.89	1.75	1.89
1.66	1.88	1.76	1.88	2.59	2.44
1.40	1.65	0.84	0.80	4.33	4.53
2.44	2.35	2.41	2.35	5.24	5.17
1.58	1.73	2.29	2.08	0.81	0.98
1.06	1.29	3.91	4.02	1.96	1.89
2.59	2.63	2.46	2.46	4.36	4.47
3.12	2.93	2.10	2.08	2.52	2.26
2.11	2.27	2.50	2.76	4.37	4.33
2.49	2.74	1.75	1.89	1.95	1.66
3.91	3.86	1.21	1.44	1.50	1.80
1.49	1.32	5.33	5.65	2.16	2.00
4.26	4.10	2.72	2.76	2.49	2.76
3.41	3.40	2.51	2.67	4.21	4.04

Inspection of the tables reveals differences ranging from 0 to 0.27, with two exceptions, in a total of 60 samples. Of this number, 46 show differences less than 0.20 per cent. while the average difference is 0.10 per cent.

This average difference is, of course, without value as an indication of accuracy unless considered in connection with the variation of each pair of parallel determinations, but where so large a percentage of duplicates fall within the limits of probable error, the average in differences of the entire number of determinations indicates in a measure the comparative accuracy of the two methods.

Considering that the figures in the tables represent first results and in no case a second determination by the same method, results by the milk-of-lime method appear quite as reliable as those obtained by the Lindo-Gladding. In the regular course of laboratory work duplicate determinations by one and the same method may easily show less closely agreeing results.

Table II shows parallel results obtained from fertilizers containing organic materials. The samples in each case were treated with dilute (1:1) sulphuric acid and incinerated before dissolving in water.

TABLE II.

Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.
2.16	2.21	1.87	1.84	2.58	2.53
1.71	1.70	1.31	1.51	2.13	2.24
2.27	2.39	2.46	2.48	1.48	1.49
1.35	1.08	1.59	1.60	2.07	1.80
1.51	1.50	2.49	2.38	2.37	2.60
1.92	1.98	1.66	1.70	2.59	2.45
2.33	2.38	2.09	2.11	2.12	1.96
3.46	3.33	1.59	1.57	2.73	2.59
1.32	1.46	2.37	2.10	2.71	2.61
2.65	2.53	2.16	2.20	2.61	2.89
1.62	1.82	2.66	2.42	2.38	2.08
1.97	1.78	1.16	1.20	2.44	2.63
2.20	2.29	3.22	3.11	2.21	2.13
1.31	1.31	2.41	2.28	2.28	2.33
3.67	3.46	3.38	3.36		

By reference to Table II we find variations ranging from 0 to 0.30 per cent. in a total of forty-four determinations. Thirty-four of these give differences of 0.20 per cent. or less, results averaging 0.06 per cent. higher by the lime method than by the Lindo-Gladding.

Table III contains results from fertilizers containing organic materials. The samples were ignited with sulphuric acid (1:1) before obtaining solutions for the lime method, while for the Lindo-Gladding, solution was obtained by boiling the unignited sample with water.

TABLE III.

Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.
1.62	1.66	2.02	2.19	2.14	2.11
0.88	0.74	1.11	1.06	1.82	1.55
1.53	1.63	1.61	1.63	3.09	3.02
1.84	2.06	2.05	2.10	2.43	2.32
2.52	2.65	2.95	2.86	2.00	2.29
1.95	2.03	1.92	2.11	2.58	2.74
2.38	2.23	1.92	2.09	2.71	2.64
1.56	1.34	1.98	1.96	1.15	1.28
2.28	2.54	1.29	1.53	2.53	2.29
1.32	1.28	2.26	2.07	1.50	1.49
1.88	1.60	2.94	3.00	4.00	3.57
0.50	0.69	2.15	2.47	1.18	1.20
1.96	1.73	1.78	1.68	2.00	2.07
2.09	2.35	1.52	1.62	1.80	1.78
2.17	2.25	1.62	1.70	1.65	1.71

## DETERMINATION OF POTASH IN FERTILIZERS.

Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.
2.38	2.43	1.83	1.64	2.63	2.37
2.88	2.60	2.24	2.21	2.97	2.94
1.43	1.26	1.95	2.04	1.84	2.14
1.93	2.14	2.37	2.56	1.65	1.81
3.70	3.46	3.41	3.52	1.54	1.30
1.35	1.48	2.68	2.80	2.85	3.13
3.03	3.02				

These results show an extreme variation of 0.29 per cent. in a total of sixty-three determinations. Forty-six of the sixty-three vary less than 0.20 per cent. while the results average 0.02 lower by the lime method.

In Table IV may be found results on fertilizers containing organic materials. Solution for both methods was obtained by boiling the sample with water. The solutions for the lime method were considerably colored by dissolved organic matter.

TABLE IV.

Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.	Lime.	Lindo-Gladding.
1.27	1.21	1.04	1.15	2.71	2.61
1.34	1.16	1.74	2.06	1.38	1.21
2.37	2.44	2.65	2.35	2.28	1.83
2.50	2.54	1.28	1.25	2.41	2.14
1.48	1.08	1.79	1.71	5.51	5.51
5.03	4.61	2.01	1.92	2.40	2.18
2.70	2.20	2.64	2.40	3.42	3.38
2.53	2.42	2.23	1.80	2.35	2.49
3.50	3.05	2.69	2.31	2.15	2.18
1.54	1.27	1.95	2.04	2.57	2.33
2.50	2.24	2.19	2.14	2.11	2.11
1.16	1.20	2.43	2.45	1.09	0.99
2.17	2.24	5.85	5.56	2.16	1.87
2.30	1.83	2.43	2.09	2.40	2.25
1.00	1.10	2.41	1.93	2.30	2.10

Although little was expected from the results obtained by the lime method under these conditions, still they show an extreme variation of only 0.55 per cent. in a total of forty-five determinations, while thirty of the forty-five differ less than 0.30 per cent., and the average difference is only 0.15 per cent. Nothing is claimed for the method when used under these conditions, but it is interesting to note that the method gives good results even when precipitation of platinum takes place in a solution considerably colored with organic matter.

## PRECIPITATION AND SEPARATION BY WEAK ORGANIC BASES.

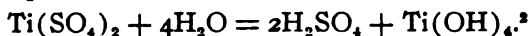
BY E. T. ALLEN.

Received January 26, 1903.

A LARGE number of organic bases are known, which may serve as quantitative precipitants of many metallic hydroxides, though they usually present no advantage over ammonia or the fixed alkalies. Of late, more especially,<sup>1</sup> some of them have found use for analytical separations, where the inorganic reagents are not applicable. We have, between the organic and inorganic bases, a nearly complete analogy. The tetrammonium compounds are well known to be highly dissociated in aqueous solution, giving, in a marked degree, the characteristic hydroxyl reactions, like the hydroxides of the alkalies and thallium. A second weaker class of bases comparable, in general, with ammonia are the paraffin amines. These also are strongly alkaline in reaction and capable of precipitating all but the strongest metallic bases, whose solubility products are too high to be reached by such concentrations of hydroxyl as these reagents afford.

A third class of bases in which the aromatic amines, quinoline, naphthyl-amine, phenyl-hydrazine, etc., may be named, have no soluble analogues in the inorganic field, though they are akin to the bases formed by the metals of the third and fourth groups of the periodic system.

With indicators they give either a faint alkaline reaction or none at all. When a metallic salt is precipitated by such a base, say aniline, the solution remains acid even when a considerable excess of the reagent has been added. It is plain, therefore, that only those bases which can be thrown down in acid solution, can be precipitated here. All chemists are familiar with the precipitation of certain hydroxides by the action of water alone. Such reactions are always reversible. We may instance the case of titanium sulphate.



<sup>1</sup> This Journal, 24, 540, and 21, 776.

<sup>2</sup> The principle involved is the same whether the precipitate be a hydroxide, or a basic salt.

The complete precipitation of the titanium evidently depends on the reduction of the concentration of free acid to a point where the titanium hydroxide is no longer appreciably soluble. Let us suppose the precipitation to be incomplete. If now we should add to the system a weak base like aniline, a certain quantity of the free acid would be converted into neutral salt, and thus the concentration of the acid would be diminished, though an appreciable quantity would always remain unless a very great excess of reagent were used, for, according to the principles of hydrolysis, the salt of a weak base must be partially decomposed by water into free base and free acid. Thus:



The precipitation of titanium will therefore go further, in fact, to completion when a proper quantity of aniline has been added, because in small concentrations of acid, titanium hydroxide is practically insoluble. The degree of the hydrolysis of the aniline hydrochloride is conditioned by temperature, by the degree of dilution, and by excess of free base. Speaking in general of this class of weak bases, it is, of course, true that the degree of hydrolysis, in other words the concentration of free acid in solutions of their salts, depends on the strength of the base. Some organic bases are so weak that they would doubtless be of no service for any quantitative precipitation, but those whose hydrochlorides are hydrolyzed to an extent of several per cent. in dilute solutions form a group well adapted for the separation of weak from strong metallic bases. For the strong bases like magnesia, the alkaline earths, etc., are incapable of existence with free acid, while the weak ones, whose salts are more or less hydrolyzed in aqueous solution, are practically insoluble in such concentrations of acid as one can readily obtain by the above means. This is the principle of most analytical separations by weak organic bases, and the most important one involved in the experimental part of this paper. Of course there are cases in which the precipitate by an organic base redissolves in excess. Thus several paraffin amines redissolve the hydroxides of aluminum, copper, silver, zinc, etc., and it is possible some of the weaker bases may yield separations on this principle, though no cases of the kind are known to me.<sup>1</sup>

<sup>1</sup> In her statement that phenylhydrazine throws down, from thorium nitrate, a "canary-yellow precipitate, easily soluble in excess," Miss Jefferson appears to be in error. See this Journal, 24, p. 546.



In the study of the separations in the sequel, it seemed of interest, not merely to determine the necessary empirical conditions, but also to inquire how much acid is freed from the salts of certain weak bases—the precipitants—under definite conditions of dilution, temperature and excess of the base. Thus the hydrolytic constant,

$$K = \frac{BOH \times HCl}{V(BCl)},$$

of aniline, and of phenylhydrazine hydrochloride was determined in N/10 solutions at a temperature of 40° C. In this way could be made an approximation to the concentration in free acid possessed by the solutions in which the separations were made—concentrations in which certain weak metallic bases remain without dissolving appreciably.

#### SEPARATION OF ALUMINUM FROM IRON.

Several years ago Campbell and Hess<sup>1</sup> described a method for precipitating aluminum in the presence of iron after the latter had been reduced to the ferrous state by sulphurous acid. The reagent used was phenylhydrazine. The results appeared satisfactory, and, as a good method for the direct determination of aluminum in the presence of iron was needed, Dr. W. F. Hillebrand suggested that I study this separation more closely, especially in regard to its application to rock analysis, where titanium is nearly always present, and sometimes zirconium. I desire in this place to express to Dr. Hillebrand my best thanks for this suggestion.

In brief, my results indicate that it is practically impossible to separate the iron completely in one precipitation. With a double precipitation, the results are good. When the quantity of precipitated alumina is large, there is apt to be a loss, which I ascribe to the long contact with the faintly acid wash solution which is necessary to remove the iron. Thus I have obtained on certain rocks results which were considerably lower than those carefully determined by difference in the usual way. On the other hand from mixtures of iron, aluminum, titanium, and zirconium salts made up from standard solutions the results have been satisfactory. This discrepancy has not thus far been explained. The method is excellently adapted to the separation of very small quantities of aluminum, such as a milligram or even less, from a

<sup>1</sup> This Journal, 21, 776.

large excess of iron, a point of considerable practical importance.

In the following tests, standard solutions of ferric and aluminum chlorides were used. The former was prepared from piano wire by dissolving in pure hydrochloric acid, filtering, oxidizing with chlorine, and driving out the excess from the hot solution by a current of air. No alumina or other bases of similar strength could be detected in this solution. It was standardized by precipitation with ammonia. The aluminum chloride was prepared by dissolving "C. P." metal in hydrochloric acid, filtering off the silicon and diluting. The exact strength was determined by precipitation with ammonia. The solution contained only a trace of iron.

To the conditions laid down by Campbell and Hess a few additions might be made. The volume of the solution may vary, according to the quantity of alumina to be precipitated, from 100 to 200 cc. It should be heated and reduced by adding saturated ammonium bisulphite. From 5 to 20 drops, according to the quantity of iron, may be used. If the solution turns deep red (ferric sulphite) it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphite itself does not reduce ferric salts, at least not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly, the oxygen of the air helps to form a little ferric hydroxide which does not always readily dissolve in the dilute acid. Finally add from 1 to 3 cc. phenylhydrazine,<sup>1</sup> according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish color, for it is not due to ferric hydroxide but to the coloring-matter contained by all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long, the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately equilibrium appears to be

<sup>1</sup> NOTE.—The reagent should, of course, be free from inorganic impurities which could disturb the results. The author found one sample, which, after persistently giving high results, was proved to contain tin, which had probably been used in its preparation.

established in a short time. The vessels need not stand more than an hour at any rate.<sup>1</sup>

#### PRECIPITATION OF ALUMINA ALONE BY PHENYLHYDRAZINE.

1 cc.  $\text{AlCl}_3 = 0.005001$  gram  $\text{Al}_2\text{O}_3$ .

	Taken.	Found. Gram.	Error. Gram.
1	50 cc. = 0.2500 gram $\text{Al}_2\text{O}_3$	0.2487	-0.0013
	25 cc. = 0.1250 gram $\text{Al}_2\text{O}_3$	0.1236	-0.0014
	5 cc. = 0.0250 gram $\text{Al}_2\text{O}_3$	0.0254	+0.0004

The tendency toward low results is here plainly visible.

#### SEPARATION OF SMALL QUANTITIES OF ALUMINA FROM EXCESS OF IRON.

The first precipitation in the following series was made in a nearly neutral solution of about 150 cc. volume. After washing out most of the iron by the phenylhydrazine sulphite solution, the precipitate was dissolved on the filter in a few cubic centimeters of hot, dilute hydrochloric acid, washed through with hot water, neutralized with ammonia and acidulated with 2 or 3 drops 1:1 HCl. The precipitate which is thrown down in a small volume of liquid by 0.5 cc. phenylhydrazine, is washed with the sulphite solution till free from iron. After blasting, the precipitate is usually pure white.

No.	$\text{FeCl}_3$ taken.	$\text{AlCl}_3$ taken.	$\text{Al}_2\text{O}_3$ found. Gram.	Error. Gram.
1	35 cc. = 0.2189 gr. $\text{Fe}_2\text{O}_3$	0.1 cc. = 0.0005 gr. $\text{Al}_2\text{O}_3$	0.0005	0.0000
2	35 " = 0.2189 " "	0.2 " = 0.0010 " "	0.0014	+0.0004
3	35 " = 0.2189 " "	0.6 " = 0.0030 " "	0.0031	+0.0001
1'	35 " = 0.2189 " "	0.7 " = 0.0007 " "	0.0008	+0.0001
2'	35 " = 0.2189 " "	1.2 " = 0.0012 " "	0.0013	+0.0001
3'	33 " = 0.1867 " "	2.0 " = 0.0020 " "	0.0019	-0.0001

#### SEPARATION OF TITANIUM FROM IRON.

As solutions of titanium chloride are quite unstable, a standard solution of the sulphate was prepared as follows: Potassium titano-fluoride of the market was twice crystallized from hot water and dried at 105° C. A weighed quantity of this compound was then heated in a large platinum crucible with excess of sulphuric acid, until free from fluorine. A very low flame should be used, or insoluble basic sulphate may form. The cooled sulphate was

<sup>1</sup> The precipitate is washed by a solution of phenylhydrazine sulphite, made by adding cold saturated sulphurous acid to a little phenylhydrazine until the crystalline sulphite first formed, dissolves in the excess. The solution has an acid reaction. Five to 10 cc. of this are used in 100 cc. hot water. See Campbell and Hess: *Loc. cit.*

then poured into excess of cold water, precipitated by ammonia, washed, and redissolved in a quantity of sulphuric acid 5 or 10 per cent. in excess of that demanded by theory, to prevent hydrolysis.

Phenylhydrazine gives a practically complete separation of titanium from iron, in two precipitations. I have never found more than traces of titanium remaining with the iron. It was sought for as follows. The iron, with any titanium it might contain after the precipitation with phenylhydrazine, was removed from the solution by ammonium sulphide, washed a few times and dissolved in nitric acid, from which solution it was subsequently precipitated by ammonia and weighed. The weighed oxide was now tested for titanium by the method described in Bulletin 176, U. S. Geol. Survey, p. 67.

TiO <sub>2</sub> found in Fe <sub>2</sub> O <sub>3</sub> .				
I.	II.	III.	IV.	V.
0.00017 gram	None	0.0002	0.0002	Trace

The same details apply to this separation as were laid down for the separation of aluminum from iron, except that here the solution may be considerably more acid before adding the phenylhydrazine. If much titanium is present, a considerable precipitate will form before the solution is completely neutralized by ammonia. When the neutral point is reached, a half dozen drops of 1:1 hydrochloric acid may be added. This quantity is frequently insufficient to redissolve all the titanium precipitate but that is a matter of no consequence.

No.	cc.	FeCl <sub>3</sub> taken.		Error.	Gram.	Ti(SO <sub>4</sub> ) <sub>2</sub> taken.	cc.	Gram TiO <sub>2</sub> .	TiO <sub>2</sub> found.	Error.
		=	Gram Fe <sub>2</sub> O <sub>3</sub> .			=				
1	35		0.1748	.....	.....	2		0.0020	0.0022	+0.0002
2	5		0.0250	0.0254	+0.0004	25		0.0246	0.0237	-0.0009
3	2		0.0100	0.0104	+0.0004	25		0.0246	0.0254	+0.0008
4	25		0.1248	.....	.....	1		0.0010	0.0011	+0.0001
5	10		0.0499	.....	.....	50		0.0492	0.0501	+0.0009
6	3		0.0140	.....	.....	50		0.0492	0.0502	+0.0010

#### SEPARATION OF ZIRCONIUM FROM IRON.

A standard solution of zirconium sulphate was used in these experiments. The raw material consisted of picked crystals of North Carolina zircon,<sup>1</sup> which were converted into potassium zircono-fluoride after the excellent method of Marignac.<sup>2</sup>

<sup>1</sup> My thanks are due to Mr. Wirt Tassin, assistant curator of the National Museum, from whom the zircon, as well as a supply of beryl, was obtained.

<sup>2</sup> *Ann. chim. phys.* (3), 60, 260.



In a recent paper by Miss A. M. Jefferson<sup>1</sup> it is stated that zirconium is not precipitated by phenylhydrazine. Now zirconia is certainly a weaker base than alumina, and, according to the principles stated in the beginning of this paper, ought to be precipitated by phenylhydrazine, the more so since, according to Miss Jefferson, it is precipitated by aniline, a base which my experiments indicate to be somewhat weaker than phenylhydrazine. It should be noted, however, that Miss Jefferson employed a cold solution of zirconium nitrate, while the experiments I have described were performed with solutions containing sulphates and chlorides or chlorides alone. As theory indicates the possibility of a difference, the following tests were undertaken: Zirconium hydroxide was prepared from the sulphate and then dissolved in dilute nitric acid. The solution was freed from most of the acid by evaporating to a volume of a few cubic centimeters, and diluted with cold water so that 1 cc. contained about 1 mg.  $ZrO_2$ . The solution contained no sulphate. In the first test, a portion of it was precipitated by a large excess of phenylhydrazine, 5 cc. to 25 cc. of the solution. After standing more than twenty-four hours, the precipitate was filtered, washed, ignited and blasted.

Found.	By ammonia.
$ZrO_2 = 0.0251$	0.0245

Twenty-five cc. of the solution with 1 cc. of the reagent gave  $ZrO_2 = 0.0241$  gram. Ammonia gave no precipitate with the filtrate. I could not discover that the zirconium hydroxide had any tendency to dissolve in excess of phenylhydrazine. The same statement may be made of aniline, which also precipitates zirconium completely.

It was thought to be of some interest to determine the behavior of phenylhydrazine with the remaining elements of this natural family, thorium and cerium.

#### PHENYLHYDRAZINE AND THORIUM.

A solution of thorium nitrate was prepared from the pure dioxide. The latter was brought into solution by fusion with potassium acid sulphate from which it was precipitated by ammonia in a form soluble in dilute nitric acid. A double precipitation was necessary to remove sulphate entirely. The nitrate was evaporated to crystallization and dissolved in cold water.

<sup>1</sup> This Journal, 24, 543.

Three portions of 25 cc. each were then precipitated as follows: No. 1 was precipitated by ammonia, washed, ignited and weighed as in an ordinary determination. No. 2 was nearly neutralized with ammonia, precipitated hot and washed with hot water. No. 3 was treated as No. 2, except that a smaller amount of reagent was added to the cold solution and the precipitate was washed with cold water. In all cases the precipitate was blasted before weighing.

ThO<sub>2</sub> found.

- 1 25 cc. contained 0.0477 gram average of three determinations by NH<sub>3</sub>.
- 2 25 " hot by phenylhydrazine 0.0477 gram.
- 3 25 cc. cold by phenylhydrazine 0.0475 gram.

The precipitated thoria was white or nearly so.

Regarding Miss Jefferson's statement<sup>1</sup> that phenylhydrazine throws down, from a solution of thorium nitrate, "a canary-yellow precipitate, easily soluble in excess," I can say that if the solution contains much free nitric acid, the precipitate is colored yellow, evidently by an oxidation product of the phenylhydrazine. The precipitate may be obscured by an excess of reagent, but there is no tendency to redissolve. Thus, in one test I employed 5 cc. of the reagent to a small volume of the thorium solution. I was at first in doubt about the result, but a careful examination showed that no thorium passed through an ordinary filter.

#### PHENYLHYDRAZINE AND CERIUM.

The remaining element in the family under consideration is cerium. It differs from the other three members, in that it is easily reducible from the quadrivalent to the trivalent state. Phenylhydrazine fails to precipitate it except in a partial way from its ceric salts, not because it is a more basic element than the rest but because it is an oxidizing agent which phenylhydrazine easily reduces to the cerous condition, and cerous oxide is a much stronger base. These statements were proved by the following experiments:

Ceric ammonium nitrate,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , was made from a preparation of cerous nitrate furnished by Merck. To separate it from any neodymium and praseodymium, it was twice precipitated by caustic potash and oxidized by a stream of chlorine, the ceric hydroxide being thor-

<sup>1</sup> This Journal, 24, 546.

oroughly washed after each treatment. The ceric hydroxide was now changed to ceric ammonium nitrate by the addition of dilute nitric acid and a little ammonium nitrate. A comparatively concentrated solution of this salt, containing considerable free acid, at once oxidized both phenylhydrazine and aniline with marked color changes, and no excess of either produced, thereafter, any precipitate.<sup>1</sup> With a dilute and nearly neutral solution, the results were different. Such a solution was obtained by evaporating one like the above to dryness in a vacuum desiccator with lime and sulphuric acid.

The beautiful orange crystals, with the small excess of ammonium nitrate they contained, were then put into solution by cold water, and after standing a day or two, filtered from a slight precipitate which had formed. The concentration of this solution was not far from 1 mg.  $\text{CeO}_2$  per cubic centimeter (20 cc. gave 0.0161 gram). 15 cc. of the solution were treated with a little phenylhydrazine and set away for twenty-four hours. Some little precipitate, composed partly of organic matter, apparently an oxidation product of the reagent, had formed, but the filtrate yielded with ammonia 0.0078 gram  $\text{CeO}_2$  out of a total quantity of 0.0121 gram originally contained in the solution. Aniline being a weaker reducing agent gave a practically complete precipitation with this solution. Only two or three very small flakes were obtained from the filtrate by ammonia.

#### PHENYLHYDRAZINE AND FERRIC SALTS.

Ferric salts follow ceric salts in their behavior, except that phenylhydrazine gives with the former almost no precipitate. This is true, at least, with both strong and weak solutions of ferric chloride. With one containing about 1 mg. per cubic centimeter, phenylhydrazine at first brings down some brown hydroxide which dissolves when the liquid is shaken, leaving only a little insoluble tarry matter. Aniline, however, gives a complete precipitation; at least the filtrate is colorless and gives no precipitate with ammonia.

#### SEPARATION OF TITANIUM FROM BERYLLIUM.

It has been shown that the elements of the quadrivalent family, Ti-Th, are, with the exception of Ce, separable from iron by

<sup>1</sup> See also Gmelin-Kraut, Vol. II, part 1, p. 508.



phenylhydrazine. Beryllium forms a much weaker base than ferrous iron, but it may be separated from titanium and zirconium in a fairly satisfactory manner by similar means. The tendency is for the beryllium also to be partly precipitated, and with sulphate solutions, especially where the quantities of the elements to be separated are considerable, satisfactory results are not obtained by two precipitations. The standard solution of beryllium employed in the work was the chloride. The source of it was beryl from Chester County, Pennsylvania. I transformed this into the double fluoride by the method which Marignac used in extracting zirconia from zircon, viz., by fusing the powdered mineral with two to three times its weight of potassium fluoride. For convenience in handling, the fused mass may be poured out in a thin sheet into a platinum basin and subsequently powdered. It is then boiled several times with successive portions of water, to which should be added at first some hydrofluoric acid. The double fluorides which silicon and aluminum form with potassium are nearly insoluble in water containing potassium fluoride, and are thus for the most part left behind. The solution is now evaporated to a small volume and allowed to crystallize. The salt is then recrystallized several times. It dissolves rather slowly in boiling water. Each time the last portion should be rejected. The compound still retains iron, which may be entirely removed by passing hydrogen sulphide through the aqueous solution, which is, of course, alkaline. The crystals may finally be dried at  $105^{\circ}\text{C}$ . It is a difficult matter to be sure of the complete absence of alumina, but the following determination indicates that the compound thus prepared is essentially pure. A weighed portion was changed into sulphate by heating with sulphuric acid, thence through the hydroxide to chloride, and finally to hydroxide again, which was ignited and weighed. To be sure that the beryllium oxide was free from sulphate, the precipitation with ammonia was, in fact, made three times. All the filtrates were evaporated to a small volume and treated with a little ammonia, which brought down a little beryllia, which was filtered and washed separately and added to the main portion. 1.2996 grams gave 0.2008 gram  $\text{BeO}$ ; calculated for  $\text{K}_2\text{BeF}_4$ , 0.1993. I am not aware that this method has been used previously to extract beryllium from beryl. For the determinations which follow, a solution of beryllium chloride was prepared as above indicated.

To separate titanium and zirconium from beryllium, it is not, of course, necessary to add any soluble sulphite. The acid solutions are merely brought nearly to neutrality with ammonia and then acidified with several drops of dilute hydrochloric acid. A double precipitation was made, and water only was used for washing. The solutions were heated but not boiled. As previously stated, the results were not so exact as in the separation of titanium and zirconium from ferrous iron.

#### SEPARATION OF TITANIUM FROM BERYLLIUM—DOUBLE PRECIPITATION.

No.	BeCl <sub>2</sub> taken.		BeO found. Gram.	Error. Gram.	Ti(SO <sub>4</sub> ) <sub>2</sub> taken.		TiO <sub>2</sub> found. Gram.	Error. Gram.
	cc.	= Gram BeO.			cc.	= Gram TiO <sub>2</sub> .		
1	10	0.0101	.....	.....	10	0.0096	0.0096	0.0000
2	10	0.0101	.....	.....	10	0.0096	0.0096	0.0000
3	5	0.0050	.....	.....	25	0.0239	0.0247	-0.0008
4	30	0.0302	.....	.....	5	0.0048	0.0069	+0.0021
5	100	0.1006	0.0960	-0.0046	100	0.0958	0.0996	+0.0038
6	95	0.0956	0.0951	-0.0005	5	0.0048	0.0054	+0.0006
7	5	0.0050	0.0049	-0.0001	95	0.0910	0.0911	+0.0001

The beryllium was determined in the filtrate from titanium by ammonia as in an ordinary determination of aluminum. Subsequent experiments showed that phenylhydrazine precipitates a large fraction of the beryllium from a solution of the *sulphate*, but none from the *chloride*. It follows that a double precipitation by phenylhydrazine from a chloride solution would give a more exact separation from titanium, than those recorded above.

#### SEPARATION OF TITANIUM FROM BERYLLIUM BY ANILINE.

No.	BeO taken. Gram.	TiO <sub>2</sub> taken. Gram.	TiO <sub>2</sub> found. Gram.	Error. Gram.
1	0.050	0.1416	0.1422	-0.0006
2	0.075	0.0944	0.0950	-0.0006

The solutions used were beryllium chloride and titanium sulphate. The mixtures were first changed to chlorides by precipitation with ammonia and subsequent solution in hydrochloric acid. From the chloride solution, a double precipitation was made by aniline.

#### SEPARATION OF ZIRCONIUM FROM BERYLLIUM.

Everything that has been said as regards the separation of titanium from beryllium applies equally well here.

No.	BeCl <sub>2</sub> taken.		BeO found.	Error.	Zr(SO <sub>4</sub> ) <sub>2</sub> taken.		ZrO <sub>2</sub> found.	Error.
	cc.	= Gram BeO.			cc.	= Gram ZrO <sub>2</sub> .		
1	5	0.0050	.....	.....	95	0.0925	0.0961	+0.0036
2	95	0.0956	.....	.....	5	0.0049	0.0061	+0.0012
3	5	0.0066	0.0040	-0.0026	45	0.0438	0.0458	+0.0020
4	45	0.0591	0.0590	-0.0001	5	0.0049	0.0052	+0.0003
5	15	0.0196	0.0187	-0.0009	45	0.0438	0.0443	+0.0005
6	35	0.0458	0.0445	-0.0013	35	0.0341	0.0359	+0.0018
7	100	0.1305	0.1290	-0.0015	50	0.0506	0.0520	+0.0014

An inspection of these tables makes it plain that a little beryllium is sure to be carried down with the quadrivalent metal, where sulphate solutions are used, but here too, as in the case of beryllium and titanium, we may confidently predict more accurate results, if chloride solutions are taken.

## SEPARATION OF THORIUM FROM BERYLLIUM.

	BeO taken.	ThO <sub>2</sub> taken.	ThO <sub>2</sub> found.	Error.
	Gram.	Gram.	Gram.	Gram.
1	0.025	0.2863	0.2847	-0.0016
2	0.025	0.1909	0.1895	-0.0014

The solutions used were beryllium chloride and thorium nitrate. Separation 1 was made with phenylhydrazine, separation 2 with aniline. Double precipitations were made in both cases. Thoria is, of course, a stronger base than titania or zirconia. From the above solutions it did not precipitate until a boiling temperature was reached and the precipitate was very slimy, like alumina when precipitated under the same circumstances. This may account for the fact that the results are a little low.

Attempts to separate aluminum from beryllium, and chromium from beryllium, and from ferrous iron, all failed. Usually the bivalent metal was carried down in considerable quantities with the trivalent one. Chromium chloride does not easily precipitate with phenylhydrazine. Many experiments tried along the above lines show that two elements when too near the same basicity can not be separated by this method, though just why the bivalent element should be partly precipitated in the presence of the trivalent is not perfectly clear.

## THE HYDROLYSIS OF ANILINE AND PHENYLHYDRAZINE HYDRO-CHLORIDES.

The degree of hydrolysis which a salt suffers in aqueous solution, may be estimated from its conductivity, the values observed

being compared with those shown by salts of the same type in which hydrolysis is negligible; or it may be calculated from the velocity of certain chemical actions which are caused by the free acid present in the salt solution. The best examples of the latter are the inversion of cane-sugar, and the saponification of methyl acetate. The last-named method<sup>1</sup> was selected in this work. A medium temperature of 40° C. was chosen. It was maintained by a thermostat of the Ostwald type, of 100 liters' capacity, which could be held within limits of about 0.2° C. for long periods. All the experiments were made with N/10 solutions of the hydrochlorides of the two bases, phenylhydrazine and aniline. Several preparations were used that there might be reasonable certainty that the saponification constants were not affected in any considerable degree by impurities. Two different samples of "C. P." phenylhydrazine hydrochloride were purified by dissolving in alcohol and precipitating by ether. One specimen of aniline hydrochloride was prepared in a similar way, and another was made from pure aniline by evaporating with pure hydrochloric acid on the water-bath. All the preparations stood a long time in desiccators with lime and sulphuric acid, before use. The reaction vessels consisted of 8-inch test-tubes which were first treated for some time with steam, then boiled with concentrated hydrochloric acid and finally very thoroughly washed and dried.<sup>2</sup> N/10 solutions of the hydrochlorides were employed in the saponification as representing on the average about the concentration of these salts in those solutions in which the separations were made. In detail, the proper quantities of the salts, *vis.*, 0.324 gram  $C_6H_5.NH_2Cl$ , and 0.361 gram  $C_6H_5.N_2H_4Cl$ , were first weighed out and transferred to the reaction tubes. The latter were then constricted in the flame at a distance of 2 or 3 inches from the open end, after which 1 cc. methyl acetate was introduced by a pipette about 2 mm. in diameter, followed by 250 cc. water free from carbonic acid. The tubes were then sealed, cooled, shaken to mix the contents, and placed in the bath. After a sufficient interval, a tube was withdrawn, chilled and opened. Its contents were then tested as follows: 1 cc. was removed by a pipette, added to a small volume of water free from carbonic acid and titrated with N/20 soda, phenolphthalein serving as an indicator. The

<sup>1</sup> Walker: *Ztschr. phys. Chem.*, 4, 319.

<sup>2</sup> Ley: *Ibid.*, 30, 229; Walker: *J. Chem. Soc.*, 68, 577.

errors in measurement were reduced to a minimum by using narrow instruments. The pipette was about 2 mm. in diameter and the 10 cc. burette, about 8 mm. During the titration, the contents of the burette were protected from the outer air by a soda-lime tube. The sodium hydroxide was prepared according to Ley,<sup>1</sup> and was proved free from carbon dioxide by titrating against N/10 hydrochloric acid, first with the aid of phenolphthalein, then with methyl orange.

1. Phenolphthalein used as indicator: 5 cc. HCl = 9.58, 9.59, 9.58, 9.60 cc. NaOH; mean, 9.59 cc.

2. Methyl orange used as an indicator: 5 cc. HCl = 9.59, 9.52, 9.58, 9.59 cc. NaOH; mean, 9.57 cc.

SAPONIFICATION OF METHYL ACETATE BY N/10 HYDROCHLORIC ACID  
AT 40° C.

25 cc. acid and 1 cc. methyl acetate were used in each test. 1 cc. acid = 0.00374 gram hydrochloric acid, as determined by sodium carbonate. The process was carried out in sealed tubes as described above:

$a_0$  = 1 cc. of the original mixture in terms of N/20 soda = 2.10.

$a_\infty$  = 1 cc. of the mixture when saponification was complete = 9.50.

$a = a_\infty - a_0 = 7.4$  = the original mass of methyl acetate in terms of N/20 soda.

Then the saponification constant for a reaction of the first order =  $K = \frac{1}{t} \log_e \frac{a}{a-x}$ .

Here, of course,  $t$  = the time, in this case measured in minutes, and  $x$  = quantity of methyl acetate changed, or acid liberated in the time  $t$ , again in terms of the soda solution. The Briggs logarithms were used in the calculation.

$$t_1 = 131 \text{ m}$$

$$t_2 = 235 \text{ m}$$

$$t_3 = 324 \text{ m}$$

$$t_4 = 363 \text{ m}$$

$$x_1 = 2.25$$

$$x_2 = 3.55$$

$$x_3 = 4.33$$

$$x_4 = 4.70$$

$$K_1 = 0.001204$$

$$K_2 = 0.001207$$

$$K_3 = 0.001180$$

$$K_4 = 0.001206$$

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$$\text{Average} = 0.00120$$

<sup>1</sup> *Ztschr. phys. Chem.*, 30, 205.

Corrected for volume, since 1 cc. methyl acetate was added to the 25 cc. acid,  $K = 0.00120 \times \frac{26}{25}$ .

Corrected for concentration, since the acid was not exactly N/10,  $K = 0.00120 \times \frac{26}{25} \times \frac{3645}{3740} = 0.001216 = 1.22 \times 10^{-3}$ .

Walker<sup>1</sup> found for the velocity constant of the same reaction at 25° C.,  $K = 0.00315$ , using normal hydrochloric acid. Ley<sup>2</sup> found at 99.7° C.,  $K = 0.00158$  as the average for N/500 hydrochloric acid, and 0.00307, average for N/250 hydrochloric acid.

If these constants are made comparable by multiplying them by their corresponding concentrations, we have:

$$kv = 0.00315 \text{ at } 25^\circ \text{ C.} - \text{Walker.}$$

$$'' = 0.01216 \text{ at } 40^\circ \text{ C.} - \text{Allen.}$$

$$'' = 0.782 \text{ (average) at } 99.7^\circ \text{ C.} - \text{Ley.}$$

Strictly these quantities should, of course, be multiplied by 2.3, because the natural logarithms were not used in the calculations.

Van't Hoff has shown that we may get some light on the change of reaction velocity with temperature if we resolve the equation  $\frac{d \log_e K}{dT} = \frac{q}{RT^2}$  (where  $K$  = the equilibrium constant,

$\frac{k}{k'}$ , of any reaction,  $T$  = the absolute temperature, and  $q$  = the

heat of reaction) into two others, *vis.*,  $\frac{d \log_e k}{dT} = \frac{A}{T^2} + B$ , and

$\frac{d \log_e k'}{dT} = \frac{A'}{T^2} + B$ .  $B$  is unknown, but often seems to be negli-

gible, in which case, assuming also that  $q$  is constant, we have  $\log_e k = -\frac{A}{T} + C$  or  $\log_e \frac{k_2}{k_1} = A \left( \frac{T_1 - T_2}{T_1 T_2} \right)$ . By the aid of this equation, we may correlate the various values of  $k$  found at different temperatures.

Substituting for  $k_2$ ,  $k_1$ ,  $t_2$  and  $t_1$ , 0.01216, 0.00315, 298 and 313 respectively,  $A = 8397$ .

Substituting 0.782, 0.01216, 372.7 and 313,  $A = 8132$ .

Considering the difference in dissociation of the different concentrations of acid, the slight variation of  $q$ , etc., the agreement seems satisfactory.  $K_T$  (the saponification constant of methyl

<sup>1</sup> *Ztschr. phys. Chem.*, 4, 324.

<sup>2</sup> *Ibid.*, 30, 530.

acetate by hydrochloric acid) may thus be approximately reckoned from the equation

$$K_r = \frac{K_{\infty}}{V} e^{8264 \left[ \frac{T-298}{298 T} \right]}.$$

SAPONIFICATION OF METHYL ACETATE BY ANILINE HYDROCHLORIDE  
AT 40° C.

$a_0 = 1.81$  = acid in 1 cc. mixture, at the beginning, in terms of N/20 soda.

$a_{\infty} = 9.30$  = free acid in 1 cc. mixture after one month in the thermostat at 40° C.

$a = a_{\infty} - a_0 = 7.49$  total acid freed by saponification in 1 cc. mixture, equivalent to the original mass of the methyl acetate in terms of soda.

$$K = \frac{1}{t} \log_e \frac{a}{a-x}$$

$$t_1 = 1330 \text{ m} \quad x_1 = \begin{Bmatrix} 2.35 \\ 2.31 \\ 2.32 \end{Bmatrix} \\ \hline 2.33 \quad - \quad 1.81 = 0.52$$

$$t_2 = 2450 \text{ m} \quad x_2 = \begin{Bmatrix} 2.80 \\ 2.85 \\ 2.81 \end{Bmatrix} \\ \hline 2.83 \quad - \quad 1.81 = 1.02$$

$$t_3 = 4290 \text{ m} \quad x_3 = \begin{Bmatrix} 3.61 \\ 3.60 \end{Bmatrix} \\ \hline 3.61 \quad - \quad 1.81 = 1.80$$

$$t_4 = 5683 \text{ m} \quad x_4 = \begin{Bmatrix} 4.20 \\ 4.23 \end{Bmatrix} \\ \hline 4.22 \quad - \quad 1.81 = 2.41$$

$$1 \quad K = 2.35 \times 10^{-3} \times \frac{26}{25} = 2.45 \times 10^{-3}.$$

$$2 \quad K = 2.60 \times 10^{-3} \times \frac{26}{25} = 2.70 \times 10^{-3}.$$

$$3 \quad K = 2.78 \times 10^{-3} \times \frac{26}{25} = 2.89 \times 10^{-3}.$$

$$4 \quad K = 2.97 \times 10^{-3} \times \frac{26}{25} = 3.09 \times 10^{-3}.$$

Now if it be remembered that the rate of reaction depends on

the concentration of free hydrochloric acid, it will be seen that the percentage of aniline salt which is hydrolyzed may be obtained by dividing these results by the constant for hydrochloric acid at the same dilution.

$$2.45 \times 10^{-3} + 1.22 \times 10^{-3} = 2.0 \text{ per cent.}$$

$$2.70 \times 10^{-3} + 1.22 \times 10^{-3} = 2.2 \text{ per cent.}$$

$$2.89 \times 10^{-3} + 1.22 \times 10^{-3} = 2.4 \text{ per cent.}$$

$$3.09 \times 10^{-3} + 1.22 \times 10^{-3} = 2.5 \text{ per cent.}$$

As there is always a constant ratio between the undecomposed part of the salt, multiplied by the volume in which it is contained, and the product of the decomposed parts, we have the well-known equation  $\frac{x^2}{V(1-x)} = C$ , where  $x$  is the percentage hydrolyzed,  $V$  is the volume in which 1 gram-molecule is dissolved, and  $C$  is the hydrolytic constant. If we take the average of  $x$  as 2.3,  $C = 5.4 \times 10^{-3}$ , or if 2 is more nearly correct,  $C = 4.1 \times 10^{-3}$ .

The strength of aniline has previously been determined by two different observers. Bredig,<sup>1</sup> using the conductivity method, concluded that 2.63 per cent. of aniline hydrochloride was decomposed in N/32 solution at 25° C., while Walker,<sup>2</sup> by the use of the sugar inversion method, obtained the value 4.5 per cent. at 60° C. in N/30 solution.

If we calculate these results to N/10 dilution by the use of the equation  $C = \frac{x^2}{v(1-x)}$ , we have :

1.48 per cent. hydrolyzed at 25° C.—*Bredig*.

2.00 " " " " 40° C.—*Allen*.

2.63 " " " " 60° C.—*Walker*.

These results indicate a nearly regular increase in hydrolysis with increasing temperature. Regarding this point not much is known, but Madsen's<sup>3</sup> results indicate that the increase may be very considerable.

#### SAPONIFICATION OF METHYL ACETATE BY PHENYLHYDRAZINE HYDROCHLORIDE AT 40° C.

$a_0 = 1.78$	$a_\infty = 10.90$	$a = 9.12$
$t_1 = 1330$	$i_1 = 0.37$	
$t_2 = 2419$	$x_2 = 0.57$	
$t_3 = 4290$	$x_3 = 1.55$	
$t_4 = 5683$	$x_4 = 2.33$	
$t_5 = 6960$	$x_5 = 3.02$	

<sup>1</sup> *Ztschr. phys. Chem.*, 13, 322.

<sup>2</sup> *J. Chem. Soc.*, 67, 582.

<sup>3</sup> *Ztschr. phys. Chem.*, 26, 294.



$$K = 1.67 \times 10^{-5} \times \frac{26}{25} = 1.73 \times 10^{-5} + 1.22 \times 10^{-3} = 1.4 \text{ per cent.}$$

$$K = 1.44 \times 10^{-5} \times \frac{26}{25} = 1.50 \times 10^{-5} + 1.22 \times 10^{-3} = 1.2 \text{ per cent.}$$

$$K = 2.38 \times 10^{-5} \times \frac{26}{25} = 2.47 \times 10^{-5} + 1.22 \times 10^{-3} = 2.0 \text{ per cent.}$$

$$K = 2.89 \times 10^{-5} \times \frac{26}{25} = 3.00 \times 10^{-5} + 1.22 \times 10^{-3} = 2.5 \text{ per cent.}$$

$$K = 3.27 \times 10^{-5} \times \frac{26}{25} = 3.40 \times 10^{-5} + 1.22 \times 10^{-3} = 2.8 \text{ per cent.}$$

Comparing these results with those for aniline hydrochloride, we note that there is an acceleration in the rate of saponification in both cases. With aniline hydrochloride, this is comparatively small; with the phenylhydrazine compound, considerable. If the periods of time had been successive instead of overlapping, the acceleration would be seen to be actually greater than the above figures indicate. If we compare the values for  $a$ , we have  $a = N/10$  hydrochloric acid, 7.4;  $N/10$  aniline salt, 7.49;  $N/10$  phenylhydrazine salt, 9.12.

This means that by some secondary reaction more acid has been formed than the methyl acetate could furnish. On this account it seems more rational to calculate the percentages hydrolyzed, from the earlier periods of the process. This leads us to the approximate values 1.5 per cent. for the phenylhydrazine salt and 2.0 per cent. for the aniline compound. Many other experiments on the saponification of methyl acetate were made with other preparations of the salts, but since all led to the same conclusions and the table given above contains the results obtained under the most carefully regulated conditions, no others have been quoted.

In calculating the values of  $K = \frac{1}{t} \log_e \frac{a}{a-x}$  for the phenylhydrazine salt,  $a$  was taken equal to 7.4.

A similar case of acceleration in the saponification of methyl acetate was noticed by Ley,<sup>1</sup> when he employed solutions of aluminum and lanthanum chlorides.

He attributed the acceleration to a secondary action between the chloride and acetic acid, setting free the more highly dissociated hydrochloric acid.

If we compare aniline and phenylhydrazine in regard to their power to precipitate the weak inorganic bases, it appears that their strength is nearly the same, but that of aniline is slightly less.

<sup>1</sup> *Ztschr. phys. Chem.*, 30, 231.

Salt.	Action of aniline.	Salt.	Action of phenylhydrazine.
$\text{Be}(\text{NO}_3)_2$	Trace of precipitate.	$\text{Be}(\text{NO}_3)_2$	Same as with aniline.
$\text{BeSO}_4$	No precipitate.	$\text{BeSO}_4$	Heavy precipitate, though not complete.
$\text{Al}(\text{NO}_3)_3$	Precipitation slow, but complete.	$\text{Al}(\text{NO}_3)_3$	Complete and much more rapid precipitation.
$\text{Al}_2(\text{SO}_4)_3$	Complete precipitation.	$\text{Al}_2(\text{SO}_4)_3$	Complete precipitation.
$\text{Cr}(\text{NO}_3)_3$	Complete, but slow precipitation.	$\text{Cr}(\text{NO}_3)_3$	Complete and rapid precipitation.
$\text{Cr}_2(\text{SO}_4)_3$	Complete precipitation.	$\text{Cr}_2(\text{SO}_4)_3$	Complete precipitation.
$\text{Ti}(\text{NO}_3)_4$	Complete precipitation.	$\text{Ti}(\text{NO}_3)_4$	Complete precipitation.
$\text{Ti}(\text{SO}_4)_2$	Complete precipitation.	$\text{Ti}(\text{SO}_4)_2$	Complete precipitation.
$\text{Zr}(\text{NO}_3)_4$	Precipitation complete, but slow.	$\text{Zr}(\text{NO}_3)_4$	Precipitation complete and considerably more rapid than with aniline.
$\text{Zr}(\text{SO}_4)_2$	Complete precipitation.	$\text{Zr}(\text{SO}_4)_2$	Complete precipitation.

These precipitations were all made in the cold, with solutions containing about 1 mg. of metallic oxide per cubic centimeter, and all were slightly acid. 15 cc. of each solution and about 1 cc. of the reagent, a large excess, were taken for each test. Where any difference is found in the behavior of the two bases, it is seen that phenylhydrazine precipitates more rapidly and in one instance, beryllium sulphate, it precipitates where aniline has no action. That both reagents bring down the same precipitates, one can scarcely doubt. They all closely resemble the hydroxides (or basic-salts), formed by ammonia, being flocculent and white or nearly so, when the reagents are free from color and the solutions are dilute. The color of phenylhydrazine is partly borne down by the precipitates. I have noticed that solutions containing free nitric acid in some quantity, form yellow or brown products which are probably oxidation products and which color the precipitates. The addition products which are formed by the action of the same bases on the chlorides of zinc, cadmium, and mercury, and by phenylhydrazine on the chlorides of cobalt and nickel as well, are entirely different in appearance; in fact they are crystalline.

Regarding the difference in the behavior of the nitrates and sulphates of the same elements, too little has been done to draw conclusions, but it will be noticed that where any difference exists, the sulphates precipitate more rapidly. The chlorides have not been systematically compared with the sulphates, but enough has been done to show that they behave similarly to the nitrates, in precipitating less rapidly and sometimes less completely than the

sulphates. This may be due to the formation of basic salts in the case of the sulphates, precipitates, which possess a different solubility from the hydroxides, or perhaps the sulphates of the organic bases are less dissociated than the chlorides.

#### CONCENTRATION OF FREE ACID IN THE SOLUTIONS PRECIPITATED BY ORGANIC BASES.

The solutions in which the previously described separations were made, are too complicated in composition to deal with directly. All contained an unmeasured quantity of ammonium salt, while some contained also several different acids. A few experiments were therefore carried out under simplified conditions.

*Experiment 1.*—100 cc. titanium sulphate, containing 0.0944 gram titanium dioxide, were precipitated with ammonia, and the washed precipitate was transferred by a jet of water to an empty beaker. A measured quantity of hydrochloric acid, greater than that theoretically demanded, was then introduced. After warming and stirring, a large part of the precipitate remaining undissolved, an excess of phenylhydrazine was poured in. The precipitate was then filtered, while the filtrate was carefully tested for traces of titanium. None was found. It is evident that we have here data which, with the value of the hydrolytic constant of phenylhydrazine hydrochloride, will enable us to calculate the quantity of free acid present. For if  $m$  equals the number of molecules of the phenylhydrazine salt,  $l$  equals the number of molecules of excess of base,  $v$  equals the volume of the solution in liters,  $k$  equals the hydrolytic constant, and  $a$  equals the degree of dissociation,

$$k = \frac{a(ma + l)}{v(1 - a)} \text{ and } a = -\frac{kv + l}{2m} + \sqrt{\frac{kv}{m} + \left(\frac{kv + l}{2m}\right)^2}.$$

Total weight of acid = 0.238.

Phenylhydrazine required =  $0.238 \times \frac{108}{36.5} = 0.704 \text{ gram} = 0.006521 \text{ gram-molecule.}$

Phenylhydrazine used = 1 cc. = 1.09 gram.

Phenylhydrazine in excess =  $1.09 - 0.704 = 0.386 \text{ gram} = 0.003575 \text{ gram-molecule.}$

$m = 0.006521$

Hence  $a = 0.001$ , *i. e.*, we have  $0.006521 \times 0.001 \times 36.5 = 0.2$  milligram of free acid in 100 cc.

$l = 0.003575$

$k = 0.00002$

$v = 0.2 \text{ liter.}$

*Experiment 2.*—In this experiment all the conditions were the same as in Experiment 1, except that only 0.8 cc. phenylhydrazine was used.

$m = 0.006521$        $a = 0.0027$ , i. e., we have 0.60 milligram of acid in 200 cc.  
 $l = 0.001555$   
 $k = 0.00002$   
 $v = 0.2$  liter.

*Experiment 3.*—To a quantity of freshly precipitated and washed alumina equivalent to 0.1257 gram  $\text{Al}_2\text{O}_3$ , was added a very slight excess of hydrochloric acid, viz., 0.280 gram; all the precipitate dissolved. At a boiling temperature, 2 cc. phenylhydrazine gave a practically complete precipitation, but the precipitate was very slimy and the conditions were not adapted to practical work. The excess of phenylhydrazine here is quite large, but other experiments with a smaller excess failed to precipitate the alumina completely.

Here       $m = 0.007672$  gram-molecule.  
 $l = 0.01251$  gram-molecule.  
 $k = 0.00002$ .  
 $v = 0.1$ .

Hence  $a = 0.00008$  and the free acid  $= 0.007672 \times 0.00008 \times 36.5 = 0.02$  milligram per 100 cc.

The concentrations of free acid in the above cases were probably a little larger than those in the solutions with which the practical work was done, for in the latter cases there was an ammonium salt which must have tended to reduce dissociation.

It is quite certain that titanium hydroxide can be quantitatively precipitated in solutions more strongly acid, but we have here, no doubt, about the same amount of free acid as in the practical work.

There is some reason to believe that the calculated values given above are somewhat too small, for I found that blue litmus paper, while it was decidedly reddened by the solutions we have just considered, gave hardly any reaction with solutions prepared by adding the calculated amount of free acid to 100 cc. distilled water.<sup>1</sup>

I am unable to explain this discrepancy. Possibly the value  $2 \times 10^{-3}$  for the hydrolytic constant of phenylhydrazine hydrochloride is too small, though one would be inclined to suspect that the method used would give high rather than low results. At all events it appears probable, in view of all the facts, that the con-

<sup>1</sup> A sensitive litmus tincture, however, reacted strongly with these solutions.

centration of free acid in the solutions we have been considering is not greater than a few milligrams in 100 cc.

#### SUMMARY.

(1) The weak organic bases, such as show little or no alkaline reaction with indicators, on account of the hydrolysis of their salts, can, of course, never completely neutralize the acid of a metallic salt. They, therefore, cannot precipitate the strong metallic bases, but only the weak ones, which are practically insoluble in very dilute acid. The precipitate may be either the hydroxide or a basic salt. All the analytical separations with these weak bases, which have been devised thus far, seem to involve this principle. The strong reducing power of phenylhydrazine gives it a particular advantage in certain cases.

(2) The work described in this paper was done with phenylhydrazine and aniline. These two bases are of about the same strength, aniline being slightly weaker. This conclusion was arrived at by the study of the saponification of methyl acetate by their hydrochlorides, and also by their power to precipitate metallic hydroxides. The saponification constants in N/10 solutions at 40° C. were found to be  $2.5 \times 10^{-3}$  for the aniline salt, and  $1.7 \times 10^{-3}$  for the phenylhydrazine salt. These numbers lead us to the values  $4 \times 10^{-3}$  and  $2 \times 10^{-3}$ , respectively, for the hydrolytic constants. This means that about 2 per cent. of the former and 1.50 per cent. of the latter are decomposed into free base and free acid, under the conditions of dilution and temperature stated above.

(3) The concentration of free acid in solutions from which the metallic hydroxides were separated must be quite small. The calculated values amounted to but a few tenths of a milligram for such volumes as 100 to 200 cc. There is some reason to think these values are too small, but it is not likely that they reach above a few milligrams in the above volumes.

(4) Aniline quantitatively precipitates the quadrivalent and weakly basic elements, titanium, zirconium, cerium and thorium, as well as the trivalent elements  $\text{Fe}^{\text{III}}$ , Al, and  $\text{Cr}^{\text{III}}$  under certain conditions, from dilute and slightly acid solutions. The solutions may be chlorides, nitrates or sulphates. The same statements apply to phenylhydrazine, except that ceric and ferric salts are

reduced by this reagent to salts of comparatively strong bases which are precipitated incompletely or not at all.

Zinc, cadmium, mercury, cobalt and nickel, when sufficiently concentrated, form difficultly soluble addition products with phenylhydrazine. With aniline, also, zinc, cadmium and mercury give similar compounds. The strongly basic elements, magnesium, barium, calcium, strontium, manganese and ferrous iron are not precipitated.<sup>1</sup>

Beryllium, when present alone, is not precipitated by aniline, nor by phenylhydrazine, except from sulphate solutions. Actual separations were worked out as follows: titanium and zirconium from iron; titanium, zirconium and thorium from beryllium. The separation of aluminum from iron proposed by Campbell and Hess was studied more closely. A double precipitation is advisable in all these separations. The separations from ferrous iron depend upon the reducing power of phenylhydrazine as well as its weakly basic nature. Aniline can not be substituted for it here, but all the separations from beryllium may be done equally well with aniline.

(5) Phenylhydrazine will accurately separate minute quantities of alumina (and probably also the weaker bases) from large masses of iron.

LABORATORY OF THE U. S. GEOLOGICAL  
SURVEY, WASHINGTON, D. C.

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### CHROM-MALONATES.

By JAS. LEWIS HOWE.

Received February 12, 1903.

COMPLEX salts of organic acids are little known. The chrom-oxalates have been thoroughly studied from the days of Mitscherlich on, and in more recent time the complex oxalates of the metals of the platinum group have been investigated by Joly, Leidié, Vèzes, and their pupils. Few, if any, other organic acids than oxalic have been examined from the standpoint of the formation of complex salts.

Several years ago a preliminary qualitative examination was made in this laboratory, by Mr. G. B. Capito and Mr. W. E. Davis, of the relations of chromium to a number of organic acids, and it

his Journal, 21, 779.

was found that several promised interesting results, among them malonic, tartronic, tartaric, racemic, lactic, and others.

Owing to pressure of other work, the investigation was laid aside until the past session, when Mr. G. R. Smiley spent some time studying the compounds of chromium with malonic acid. The investigation has now led in quite a different direction, and, as there is no prospect that the chromium salts will be further studied in this laboratory, the results obtained by Mr. Smiley are published at this time.

The method used in the study of the chromium malonates was to prepare chromium hydroxide by the action of ammonium hydroxide upon a solution of pure chromium chloride, the green precipitate being washed by decantation until the wash-waters showed no further trace of soluble salts. This process took several weeks. This chromium "mud" was preserved in a moist condition. Definite quantities of the hydroxide were dissolved in solutions of malonic acid of varying strengths. When it was desired to form salts, an excess of malonic acid was used, and this excess neutralized by the base. The salts, with the exception of that of pyridine, do not crystallize well, and it was in most cases difficult to prepare enough of the pure salt for analysis.

Two chrom-malonic acids were found:  $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$ . These must undoubtedly be looked upon as true complex acids, and correspond to the chrom-oxalic acids. The pyridine salt of the monobasic chrom-malonic acid was obtained in fine crystals, as well as a very similar potassium salt, which probably has the same composition. Small quantities of a similar ammonium salt were obtained, but not enough for analysis. It was always accompanied by a salt, very different in appearance, consisting of thin blue plates. This blue salt reminds one of the tribasic chrom-oxalates. A single sample, appearing pure under the microscope and weighing 0.09 gram, gave 19.95 per cent. chromium, which would indicate that it was not a salt of the tribasic acid. A similar blue salt appeared in working with other acids and also with cobalt salts.

The cesium and rubidium salts obtained are unlike the pyridine and potassium salts, and unlike each other. They are not of a simple formula, and the amounts obtained were insufficient to determine the composition of the salts. The rubidium-chromium ratio was 4:5, and the cesium-chromium ratio 1:7. The rubidium

salt is orthorhombic and strongly pleochroic, while the cesium salt shows no pleochroism.

Work is at present being carried on in this laboratory on the double salts of cobalt with organic acids; the cobalt malonates prove to be easily oxidizable to cobalti-malonates.

*Chrom-malonic Acid, Monobasic*,  $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ .—Formed by the action of malonic acid solution on chromium hydroxide. Pink crystals, not pleochroic, rather insoluble in cold water, soluble in hot water. The solution is acid and the chromium is not precipitated by ordinary reagents. It forms salts on neutralization by alkalis.

	Calculated for $\text{HCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ .	Found. Per cent.
Chromium.....	17.74	18.08
Water.....	12.32	13.97

*Chrom-malonic Acid, Tribasic*,  $\text{H}_3\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$ .—Formed by warming chromium hydroxide with excess of malonic acid in solution. Fine, pale pink powder, soluble in water. Similar in properties to the monobasic acid.

	Calculated for $\text{H}_3\text{Cr}(\text{Mal})_3 \cdot 3\text{H}_2\text{O}$ .	Found. Per cent.
Chromium.....	12.55	12.41
Water.....	13.00	12.98

*Pyridine Chrom-malonnate*,  $\text{PyrCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ .—Formed by neutralizing a solution of chromium in excess of malonic acid, with pyridine. Monoclinic crystals, showing base, prism, clinopinacoid and pyramid; trichroic, exhibiting pink, salmon, and violet. Rather difficultly soluble in cold water, but easily soluble in hot water, from which the salt crystallizes readily.

	Calculated for $\text{PyrCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ .	Found.	
		I. Per cent.	II. Per cent.
Chromium.....	14.00	13.80	13.99

*Potassium Chrom-malonnate*.—This salt resembled, both in manner of formation and in properties, the pyridine salt, exhibiting the same pleochroism and the same crystallographic form. The chromium-potassium ratio in two analyses was found to be 1:1.05 and 1:0.93, and the chromium-water ratio in one analysis 1:1.75, making the probable formula of the salt  $\text{KCr}(\text{Mal})_2 \cdot 2\text{H}_2\text{O}$ , similar to that of the pyridine salt.



## NEW BOOKS.

### THE TEACHING OF CHEMISTRY AND PHYSICS IN THE SECONDARY SCHOOL.

BY ALEXANDER SMITH, B.Sc., PH.D., Associate Professor in the University of Chicago, and EDWIN H. HALL, PH.D., Professor in Harvard University. New York, London, and Bombay : Longmans, Green, and Co. 1902. Crown, 8vo. xiii + 377 pp. Price, \$1.50.

This book has not an uninteresting page in it, and is "as full of meat as an egg" when it is in the hands of those for whom it is intended, "teachers who are earnestly seeking for improvement" (editors' note), and others who have some knowledge, the more the better, of chemistry and physics. To such, the volume fulfils its share of the mission of the American Teachers' Series, of which it forms a part, that of being a teacher's help.

"The authors of the separate parts on chemistry and physics have conferred frequently \* \* \* \* \* to avoid unnecessary duplication \* \* \*. In a few instances, however, the divergence between the opinions of the authors seemed to make it desirable that each should present his own" (editors' note).

The foregoing will indicate, in part, why nearly two-thirds of the book is written by the chemist and the remainder by the physicist. The chemistry comes before the physics in the book, the chemist concluding, however, that physics should come before chemistry in the laboratory and the classroom.

While primarily intended for teachers in the secondary schools, the reading of the book will more than repay the college or university instructor. The parts given to chemistry and physics are full of suggestions but differ in treatment and in the amount of detail and emphasis given to similar topics in the two sciences.

The work begins with a discussion on the value of science in general, and chemistry and physics in particular, in a scheme of secondary education. It presents the conflicting views in a clear, comprehensive and satisfying, if not satisfactory, way. This is followed with considerations regarding the place and sequence of chemistry and physics in a curriculum. Then follows the character and method of the instruction in chemistry, in the classroom and the laboratory; the subjects of the courses; the equipment of the laboratory in apparatus, in literature, and in first aid in case of accident; with an excellent bibliography of chemistry for the teacher first and then, to a limited extent, for the pupil in addition

to the bibliography at the beginning of each chapter and the notes and references which are found on nearly every page; and last and greatest, the equipment and development of the teacher.

The matters discussed under physics are, *mutatis mutandis*, the same as those under chemistry, without following the same order.

While every one will not agree with the authors in all their views, it will be generally admitted that these views are urged with ability, earnestness and moderation, and in their endeavor to show how chemistry and physics can be made of more intellectual benefit in a course of instruction there will be few that will deny that they have succeeded and at the same time made a book that will repay careful study from cover to cover. W. G. BROWN.

THONINDUSTRIE-KALENDER, 1903. WEIHNACHTSBEILAGE DER THONINDUSTRIE-ZEITUNG, BERLIN.

The publishers of the *Thonindustrie-Zeitung* have distributed to their patrons their annual calendar, in two parts, for 1903.

Part I, bound in linen, as is usual with such publications, is largely in diary form, but contains in addition 69 pages of maxims for clayworkers, in very concise form, which apply not only to the technical but also to the management of the administrative and mechanical sides of the clay industries. Although many of the observations are truisms, they are all more or less suggestive and might bring about a decided improvement in the results attained in any of our own clay industries were they translated and put into the hands of managers, superintendents and foremen.

Part II, in paper, 450 pages, opens with instructions as to the proper manner of examining clay deposits by borings and cuts, pointing out the necessity for so doing, and the methods of determining the depth, extent, and character of the material in any deposit before attempting to develop and use it. Apparatus such as calorimeters, that for the examination of flue gases, draft indicators in their various forms, flue thermometers, alarm clocks for the guidance of stokers at the kilns, registering clocks for the control of the firemen and others, are described. The manner of determining the completion of the burning processes from the shrinkage of test-pieces and of the temperature of the kilns, by means of the very useful Seger cones, and by pyrometers of the electric type, with tables showing the temperatures with which cones of various

numbers correspond, are explained. Paragraphs on hygrometers and their uses, the control of temperature in drying chambers, methods of determining soluble salts in clays for the prevention of efflorescence in the finished products, for the water capacity of clays, for their examination for uniformity by elutriation, for the determination of voids or volume weight, and their binding properties follow. Tests for the amount of solid glazing material necessary in glazing, for determining the crushing strength of the finished products, their loss from attrition and their resistance to impact and weathering are noted. The use of the Deville furnace for testing the fire-resisting quality of clays and the determination of their shrinkage or contraction in burning is described. The apparatus for all these determinations or tests and for the control of the burning processes are furnished by the laboratory of the editors. Much of it could no doubt be introduced into the clay-working industries of the United States with success.

The remainder of the contents of the second part of the calendar is of purely local interest in Germany, unless it be a list of books, 475 in number, relating to the various industries in which clay is employed, which are sold by Seger and Cramer, 6 Kruppstrasse, Berlin, N. W. 5.

To all engaged in the clay industries, especially the production of brick and terra cotta, who have a knowledge of the German language, the calendar will be found to be, at least, suggestive, although largely an advertisement of the wares of Seger and Cramer.

CLIFFORD RICHARDSON.

**LEAD SMELTING : THE CONSTRUCTION, EQUIPMENT, AND OPERATION OF LEAD BLAST-FURNACES, AND OBSERVATIONS ON THE INFLUENCE OF METALLIC ELEMENTS ON SLAGS, AND THE SCIENTIFIC HANDLING OF SMOKE.** BY MALVERN WELLS ILES, PH.D., some time Assistant Instructor Qualitative Laboratory, School of Mines, Columbia University; Chemical Fellow, Johns Hopkins University; Assayer and Chemist, Grant Smelting Works, Leadville, Colo.; Metallurgist, Omaha and Grant Smelting Works, Denver, Colo.; also Holden Smelting Co., Denver, Colo.; Superintendent Globe Smelting and Refining Co., Denver, Colo. John Wiley and Sons. 1902. 228 pp.

This book, in which the author has recorded the experience of many years of actual contact with smelting operations, is a very complete discourse on the subject told in a conversational style without any attempt at literary embellishment, and the student

will find here what he wants to know : how to carry into practice the principles he may have received elsewhere.

Owing to the manner of presentation there is more or less repetition, but perhaps this is advantageous rather than otherwise, inasmuch as this occurs while considering different phases of the subject.

After a general discussion of the blast-furnace and its management, suggestions as to drawings and specifications are given, including a full discussion of the inner lines of the furnace. This part of the work is fully illustrated, and dimensions are given, also a historical sketch of the changes which have taken place from time to time; this is followed by details of the foundation, the crucible, the water-jackets and the superstructure.

The power plant is fully discussed, and the equipment of the plant with tools and implements is treated in much and valuable detail.

After some suggestions as to "blowing in," the calculation of charges is dealt with, followed by suggestions as to the general supervision and operation of the plant. Fifteen pages are devoted to wall accretions and influence of metallic elements. The results of the smelting operations, the composition of slags, bullion, etc., and the production of antimonial lead is fully dealt with; there is also a short chapter on roasting furnaces. The balance of the book, some sixty pages, is taken up with a discussion of "smoke" in which "the aim has been to show how the stupendous values heretofore lost in smoke can be saved by filtering through cloth." The author strongly advocates this use of cloth for collecting fumes.

Any student aspiring to the management of a smelter, particularly a lead smelter, should study this book. It will prove helpful to all who desire some knowledge of this branch of metallurgy.

WM. HOSKINS.





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OF AGRICULTURE, No. 48.].

## ON THE CAUSE OF THE CEMENTING VALUE OF ROCK POWDERS AND THE PLASTICITY OF CLAYS.

BY ALLERTON S. CUSHMAN.

Received February 17, 1903.

IN the course of the investigation of rocks as road-building material, it early became apparent that in addition to the hardness, resistance to wear, and other physical, mechanical, and economical conditions that required consideration, the binding power, or as it has come to be called, the cementing value, was one of the most important factors in deciding as to the nature and value of the material.

The description of methods of reducing the materials to powders, the formation from these powders of briquettes under constant pressure, and the subsequent impact testing by which the cementing value is obtained, has already been thoroughly described by Mr. L. W. Page,<sup>1</sup> to whom the development of the study of the cementing value of rocks and the methods of impact testing is due. An outline description of the methods employed is all that is necessary here. The stone or other material is ground in a ball mill until it passes a screen with 40 meshes per centimeter

<sup>1</sup> Report Massachusetts Highway Commission, 1900.

(100 per inch). This sifted powder is then mixed with sufficient water to make a stiff "dough." After standing twenty-four hours, cylindrical briquettes are made of standard size (25 mm.  $\times$  25 mm.) at a standard pressure of 100 kilograms per square centimeter. This is done in a specially designed hydraulic press. The briquettes are then dried in an air-bath at 100° and tested in an impact machine which delivers a standard blow of 1 kilogram, falling 1 cm. The cementing value is measured in this laboratory by the average number of standard blows that a series of briquettes made from a rock powder will stand. The tests on many hundred samples, including clays, gravels and rocks of every description have shown a range of cementing values varying from those which will stand several thousand blows down to those that will barely stand one. A careful scrutiny of recorded tests in connection with the nature and chemical composition of a given material does not reveal the reason for the phenomenon. Rocks which, on chemical analysis, show themselves essentially identical in composition frequently vary widely in cementing value.

We are at once reminded of the great variation in plasticity which has been found in the case of clays. That the plasticity of clays is a phenomenon allied to, if not identical with, the binding power of rock dust there seems to be no doubt. The same property which makes a rock dust bind makes it form a plastic mass when worked up with water. It has never been positively decided whether there is a definite combination constituting the essential basis of all substances to which the name clay is applied.<sup>1</sup> If there is, however, one quality which marks and characterizes a clay and distinguishes it from other finely divided material found in nature, it is plasticity. The classification of materials, according to the size of the particles into silts and clays, is in the opinion of the writer incorrect. Powdered glass in the finest state of subdivision in which it can be obtained by elutriation has no cementing value whatever, and the same thing is true of the powders obtained from the natural glasses and semiglasses represented by some of the igneous and metamorphic rocks.

If we compare a plastic powder with a non-plastic one, nothing is explained when we say that in the former case the particles cohere, while in the latter they do not. The problem still remains to discover, if possible, the reasons for this cohesion. No adequate

<sup>1</sup> Compare Century Dictionary.



explanation of the plasticity of clays has as yet been advanced. So high an authority as Dr. Heinrich Ries<sup>1</sup> has left the subject open by his statement that: "Plasticity, *whatever its cause*, is an important property from a commercial standpoint and interesting from a scientific one." The same authority presents to us the various theories that have from time to time been advanced to account for the phenomenon, and finally decides on a combination of the two theories, of Cook<sup>2</sup> and Olchewsky.<sup>3</sup> "Cook considered plasticity to be due to a plate structure present in the clay, the plates sliding over each other and thus permitting mobility in the mass without cracking. He further found that in the kaolins the plates of kaolinite were frequently collected in little bunches, and that, after these were rubbed in a mortar, in order to tear apart the plates, they showed increased plasticity. Olchewsky was probably the first to suggest that the plasticity and cohesion of a clay are dependent on the interlocking of the clay particles and kaolin plates, and in this connection used the briquette method of testing the plasticity, or rather obtaining a numeric expression of it by testing the tensile strength of the air-dried clay."<sup>4</sup> The above explanation, if explanation it can be called, is far from satisfactory. In fact we are no nearer an understanding of the phenomenon when we say that clay particles "interlock" than when we say that they cohere. Moreover, simple plate-shaped particles do not, *ipso facto*, lead to high cementing value and plasticity, as many substances, such as mica, talc, graphite, etc., do not yield plastic powders. It has been claimed that the explanation is to be sought<sup>5</sup> in the size as well as the shape of the particles, but, though undoubtedly both these elements enter into the problem, it is none the less true, as will be shown later, that at no obtainable degree of fineness does a non-plastic powder begin to show plastic qualities. Orton,<sup>6</sup> commenting on the work of Cook, says: "Clays already naturally plastic show no plates at all, only a homogeneous matrix. These points indicate that the plasticity of a clay depends on the extent to which the tendency to a crystalline structure has been destroyed in the treatment that the clay has received." It is well

<sup>1</sup> Bull. N. Y. State Museum, 38, No. 7, p. 544 (1900).

<sup>2</sup> N. J. Geological Survey, (1878); Clays of N. J.

<sup>3</sup> *Topf. u. Zieg. Ztg.* (1882), p. 29.

<sup>4</sup> Ries: *Loc. cit.*

<sup>5</sup> Compare G. P. Merrill's "Rock, Rock Weathering and Soils."

<sup>6</sup> Orton: Geol. Surv. of Ohio, 7, 1.

known that the plasticity of many clays is increased by soaking and kneading with water, and the same thing is noticed in the case of the cementing power of rock dusts, granting that there is a certain plasticity to begin with. Starting with a non-plastic powder no amount of working-up will give it cementing power. Any further discussion of these points will now be deferred until certain results have been presented which bear directly upon the cementing power of rock powders.

#### THE CEMENTING VALUE OF ROCK POWDERS.

It was realized from the beginning of the investigation that the phenomenon of the cementing power of rock dusts was possibly the result of several if not many causes. Among those which might be expected to have more or less influence, may be mentioned:

(1) Solubility, however slight, of the material or of certain ingredients of the material.

(2) Size and shape of the particles.

(3) Chemical reactions set up on moistening the powders, as in the cases of Portland cements, mortar, etc.

(4) Crystalline forces operating under either 1 or 3, as in the cases of plaster-of-Paris, mortar, cements.

(5) Physical nature or condition of the particles and their relations to water: (a) Unbound water; (b) hygroscopic water; (c) water of crystallization; (d) water of constitution, or combination.

After many experiments in this laboratory, some of which are detailed in the following pages, the conclusion was reached that, although the causes put down under the first four headings are to a certain degree operative in many cases, and even perhaps of paramount importance in exceptional ones, it is under the fifth heading that the true cause of cementing power and plasticity must be sought.

If a rock powder is ignited at a temperature at which all the water of combination is expelled, the cementing power is invariably totally destroyed. This is also true as regards the plasticity of all grades and varieties of clays. No better indication could be had that the binding power is a function of the combined water or of some condition of the particles which is invariably accompanied

by the presence of combined water. Early in the investigation the idea had suggested itself that there must be a physical difference in the nature of the particles. Powders which cement well, must be composed of particles which present to one another more or less "sticky" or adherent surfaces. As a matter of fact, a trained eye can at once detect a powder that is likely to give a high cementing value. A plastic powder when poured on a flat surface will form a more or less cone-shaped heap, while a non-plastic powder, to use the language of the clay worker, "squats." Most authorities have rejected the notion<sup>1</sup> that water of combination conditions the plasticity, for the simple reason that many totally non-plastic earthy deposits and minerals have a high water content. The difficulty has probably arisen from a failure to distinguish *different kinds* of water of combination. The whole question of combined water in inorganic materials is a most interesting one and will be more fully discussed later on.

In the earlier experiments, four road-building materials were selected, which, while essentially similar in geological character and chemical composition, had shown a wide variation in cementing value. The number, analysis, cementing value, specific gravity and weight of the dry 25 mm. briquettes are given in the table below.

TABLE I.

	No. 441.	No. 341.	No. 342.	No. 414.
H <sub>2</sub> O.....	5.20	4.73	3.00	0.20
SiO <sub>2</sub> .....	83.22	83.35	88.06	95.90
Al <sub>2</sub> O <sub>3</sub> .....	7.75	9.53	6.00	2.60
Fe <sub>2</sub> O <sub>3</sub> .....	3.10	2.23	2.34	1.05
CaCO <sub>3</sub> .....	0.75	trace	0.00	0.50
MgCO <sub>3</sub> .....	0.00	0.00	0.00	trace
	100.02	99.84	99.40	100.05
Cementing value .....	297.0	101.0	74.0	2.0
Specific gravity of powder ...	2.3	2.6	2.5	2.5
	Grams.	Grams.	Grams.	Grams.
Weight dry briquette.....	22.5	23.6	21.0	18.8

A study of these records shows that the degree of hydration, in so far, at least, as these four samples are concerned, has followed the order of the cementation. In addition to this, it is seen that the respective weights of the 25-mm. briquettes are not in the ratio of the specific gravities. In other words, some rock powders are

<sup>1</sup> Compare Cook: *Loc. cit.*, p. 288.

apparently more compressible than others. In so far as the writer is aware, little or no attention has been given to the subject of the compressibility of rock powders; it is not even known what bearing water of combination has on the volume relations of powders. In order to pursue this subject, it was decided to further investigate the samples, the analyses of which have been given above. Portions of the rock powders were ignited at a red heat until completely dehydrated; a series of briquettes were then prepared by weighing exactly 20 grams of each of the powders, both raw and ignited. These briquettes were then carefully measured, and determinations of the specific gravity of the powders made. The results are contained in the following table.

TABLE II.

No.	Water. Per cent.	sp. gr.	Height of 20- gram briquette.	Cementing value.	Compression.
44I.....	5.20	2.3	22.2	297	7
44I ignited ....	0.00	2.5	29.0	2	—
34I.....	4.73	2.5	21.2	101	2.8
34I ignited ....	0.00	2.6	25.2	2	—
342.....	3.00	2.5	23.8	74	2.4
342 ignited ....	0.00	2.5	27.0	2	—
414.....	0.20	2.5	26.6	2	—
414 ignited ....	0.00	2.4	28.9	2	0.2

An inspection of the above table shows that the briquettes made from ignited powder are invariably larger than those made from raw powder, and that this difference in height is not entirely accounted for by the slight difference in specific gravity. Assuming that the water of constitution is so included in the particles of the raw powder as not to add materially to their bulk, a correction must be applied for this. For instance, in the case of No. 44I, 5.2 per cent. of the 20 grams weighed, or 1.04 grams, consisted of combined water. In No. 44I ignited, this proportion of the weight is substituted by material which certainly adds to the volume. In this table the values in the column headed compression are obtained by applying corrections for the change in specific gravity and loss in water. The following formula gives at once the compression from the data involved:

$$C = B - \left( \frac{Aa}{b} + \frac{yB}{100} \right),$$

where A and B are the respective heights of the raw and ignited

briquettes,  $a$  and  $b$  the corresponding specific gravities, and  $\gamma$  the percentage of water of hydration.

It appears from these results, which have been confirmed by many others not here given that plastic powders molded into briquettes under a given pressure apparently suffer a certain compression which is not shown by the material after the plastic condition has been destroyed by ignition: We have now to inquire if any reason can be found not only for this compression but for the fact that it seems to accompany the plastic condition.

Compressibility may be conditioned by: (1) Porosity and plasticity of the particles which would allow of their being "squeezed" into closer contact and configuration. (2) Shape and size of the particles governing their resistance to close contact and the inclosure of voids.

In this work it was found that the ignited powder always contained a much larger proportion of impalpably fine dust than the raw hydrated powders. This is shown not only by microscopic examinations but proved by dropping the respective powders into water, when it is easily seen that the former contains a greater proportion of fine material which remains longer in suspension.

It is conceivable that a hydrated material may possess a porosity so fine that the magnitude of the interstitial spaces is submicroscopic, perhaps not far removed from that of the water molecules themselves. The heating by ignition of a powder consisting of such hydrated particles would have a bursting or disrupting effect upon the particles which would thus fall down to a more impalpable dust.<sup>1</sup>

In order to investigate the effect of size of particle on the volume of briquettes it was decided to prepare glass powders of different degrees of fineness. A quantity of the best French plate glass was accordingly powdered in the ball mill and sifted through a 0.25-mm. mesh screen. A quantity of the sifted powder was shaken up with a large excess of distilled water and allowed to settle for ten minutes. The portion in suspension was then decanted to another vessel and allowed to settle again for thirty minutes; the decantation was then repeated and the third or finest portion allowed to settle completely. The three portions were thoroughly dried in an air-bath, and the three powders examined under a high-

<sup>1</sup> At the time at which the above was written the author was not familiar with the interesting work of Van Bemmelen on the dehydration of inorganic colloids (the so-called hydrogels), or with the miscellian theory of Nageli.

power microscope fitted with a micrometer eye-piece, with a view to getting some notion of the comparative size of the particles in the respective samples. As the size of the different particles was in no case uniform, the best that could be done was to measure the largest particle that presented itself in each field and then select one that seemed more nearly to represent an average; 20-gram briquettes were then made from each of the three powders, and carefully measured. The cementing value is given in each case to show that it does not increase with the fineness of the particles, if a non-plastic powder is being dealt with. The results are given in the following table:

TABLE III.

Sample.	Approximate size of powders. mm.	Amount of water used in making briquettes. cc.	Height of briquette. mm.	Cementing value.
Coarse.....	maximum 0.2	4	29	1
	average 0.025			
Medium .....	maximum 0.050	4	34	1
	average 0.017			
Fine .....	maximum 0.012	4	36	1
	average 0.004			

It may be questioned whether the difference in the observed volume of the briquettes could be occasioned by a difference in the specific gravity of the various powders. The extreme compression observed between the minimum and maximum volume in these glass briquettes is 9.5 mm.; this corresponds to a calculated difference of 0.7 of a unit in the specific gravity. That is to say, if the powder had a specific gravity equal to 2.5, the finest would have to have a specific gravity equal to 1.8 in order to account for the variations. It is impossible to believe that such a homogeneous material as plate glass could be separated into portions of such widely differing gravities, and, moreover, in spite of the difficulties attending the determination of the specific gravity of very fine powders, such wide differences could not escape experimental detection. As a matter of fact, determinations carefully carried out showed little or no deviations in specific gravity.

The question then is, how are we to explain these results? As far as the writer is aware there is little information available in the literature on the volume relations of fine powders under given pressures, although much has been said on the subject when it is a question of a far larger order of magnitude, *i. e.*, in relation to

the size and shape of broken stone and pebble in concrete mixtures. It is possible, of course, that the finer powders enclose voids that resist compression more than do the coarser and more angular particles. Again it may be considered that in the form of a solid cylinder, glass is occupying the smallest volume it can occupy. If the glass is crushed to fragments these fragments can be compressed to a certain degree by a given pressure; if we break these fragments still smaller, the resulting fragments, however tiny, are made up of particles arranged in more compact order and in less space than they could be arranged again if once set free. From purely theoretical consideration, therefore, we may say that in reducing the fineness of a powder we are approaching an ideal condition of unit particles which can not be forced by any ordinary pressures into the same space they occupied as part of fused masses. Whatever the proper explanation of these results may be, it is certain that an increase in the amount of impalpable dust of the smallest possible magnitudes apparently decreases the compressibility of the material by a given pressure. Turning again to the results on rock powders we are led to the conclusion that the driving off of water of combination breaks up the particles to a finer dust, also that this destruction of the particles leads to loss of plasticity.

As there were on hand in this laboratory a large number of thoroughly air-dried samples of rock powders and clays, of which the cementing value was known, it was decided to determine the water content of these, with a view to seeing if indeed any relation could be traced between cementing value and water of combination. The determinations were made by igniting the powders in a platinum boat contained in a hard glass tube and absorbing the water set free in a weighed sulphuric acid bulb-tube. The results are contained in the following tables:

TABLE IV.

*Dolomites and Limestones.*

No.	Cementing value.	Water. Per cent.	Name.
451.....	9	0.40	Dolomite.
665.....	10	0.30	Dolomite.
537.....	10	0.50	Dolomite.
663.....	12	0.35	Limestone.
489.....	13	0.14	Calcite.
470.....	16	0.48	Dolomite.
487.....	26	0.38	Limestone.

No.	Cementing value.	Water. Per cent.	Name.
343.....	32	0.40	Dolomite.
515.....	38	0.40	Limestone.
664.....	41	0.40	Limestone.
503.....	54	0.58	Limestone.
666.....	58	0.66	Limestone.
347.....	95	0.34	Limestone.
424.....	99	0.64	Limestone.
336.....	158	1.00	Limestone.
361.....	158	2.26	Clay limestone.
462.....	161	1.20	Dolomite.
377.....	195	1.20	Limestone.
557.....	595	6.10	Clay limestone.

*Miscellaneous Rocks.*

No.	Cementing value.	Water. Per cent.	Name.
468.....	2	0.00	Gneiss.
580.....	2	0.43	Gravel.
414.....	2	0.20	Metamorphic silicious rock.
499.....	4	0.02	Quartzite.
652.....	8	3.2	Gravel.
451.....	9	0.40	Gravel.
465.....	14	0.81	Gravel.
651.....	17	1.30	Gravel.
372.....	25	0.56	Gneiss.
592.....	41	1.50	Gravel.
342.....	74	3.00	Silicious chert.
536.....	77	0.68	Gravel.
341.....	101	4.73	Gravel.
335.....	110	1.90	Trap rock.
361.....	158	2.26	Calcareous clay.
441.....	297	5.20	Gravel conglomerate.
396.....	327	2.00	Felsite.
534.....	475	5.00	Red clay.
398.....	577	2.50	Rhyolite.

TABLE V.—DIABASE TRAP ROCK.

No.	Cementing value.	Water. Per cent.	Average.	
415.....	2	0.81	Low group	{ Cementing value, 6.00 Water content, 0.82
420.....	6	0.81		
354.....	10	0.84		
405.....	19	1.14	Middle group	{ Cementing value, 25.00 Water content, 1.35
350.....	19	1.46		
566.....	38	1.45		
357.....	72	1.80	High group	{ Cementing value, 87.00 Water content, 2.04
517.....	76	1.67		
467.....	91	2.81		
335.....	110	1.90		



An inspection of these results shows at a glance that high cementing values show a decided tendency to accompany a high water content. At the same time we see that there are several exceptions revealed, and it is probable, that an even greater number of results would show other discrepancies, as it is well known that many minerals with high water content do not yield plastic powders. On the other hand, if a certain kind of water of combination invariably accompanies the plastic condition, this active water would be added to the inactive and an explanation furnished, not only for the general tendency, as shown above, but also for the exceptions to it.

We have to inquire what is meant by water of combination. Probably no term in chemistry has been more loosely used than this. Ordinarily speaking, it refers to the water which is contained in a substance in such a way that no amount of drying at 100 C. is able to dislodge it. In this way it is differentiated from unbound water and probably from hygroscopic moisture. Such a definition, however, would include as a general thing water of crystallization, which is not usually meant when we speak of water of combination. It might be subdivided into chemically bound or hydroxyl water, and physically bound or included water, but as a matter of fact, so little is known about the relation of water to structure, that classification is at present impossible.

The question of opalline or zeolytic water has been much discussed<sup>1</sup> but recent work seems to indicate that the combined water in these cases exists in a physically rather than in a chemically bound condition. Even the water in the metallic hydroxides to which we assign arbitrary formulas has fallen under grave suspicion.<sup>2</sup>

In 1893 Van Bemmelen began the publication of a series of researches<sup>3</sup> on the inorganic colloids or "Hydrogels". Nearly all metallic oxides and many salts have the power of entering into that peculiar hydrated, non-crystalline condition which Graham<sup>4</sup> in 1861 denominated colloid or glue-like. The special hydrogel

<sup>1</sup> See Friedel: *Bull. Soc. Min.*, 19, 14, 94 (1896); also *Compt. Rend.*, 122, 1006.

<sup>2</sup> "Die Frage scheint erlaubt, wann endlich in den Handbüchern und in den Abhandlungen von Hydraten mit chemischen Formeln zu sprechen aufhören wird, bei Substanzen, die nur eingetrocknete Hydrogels sind. So begegnet man, z. B., überall dem Eisenoxydhydrat mit der falschen Formel  $\text{Fe}_2(\text{OH})_6$ . Diese kristalloidale Verbindung wurde noch nie bereitet." V. Bemmelen und Klobbie: *J. prakt. Chem.*, 46, 497-529 (1892).

<sup>3</sup> *Ztschr. anorg. Chem.*, 8, 466; *Ibid.*, 13, 233; *Ibid.*, 18, 14; *Ibid.*, 20, 185; *Ibid.*, 22, 313.

<sup>4</sup> *Phil. Trans.* (1861), p. 183.

which Van Bemmelen studied most minutely was that of silicic acid, although his researches include the oxides of copper, tin, iron, alumina, etc., etc. As a result of these extensive investigations the author cited adopts the suggestion of Nageli of the micellian structure of colloids, that is to say, that these curious substances consist of heterogeneous molecular complexes which possess a submicroscopical, web-like, porous formation, one of the distinguishing characteristics of which is the peculiar relation to and dependency upon water which they exhibit. The water content of these hydrogels varies continually with the temperature and the vapor-pressure of the atmosphere in which they find themselves. Dried at high temperatures up to a certain critical point, they will loose nearly all their water, only to take it back again eagerly when allowed to cool in free air or in moist atmospheres. This dehydration and rehydration can be repeated indefinitely unless the temperature of drying is carried too high, when the faculty is gradually lost and finally destroyed. We have here to do with a certain kind of water of combination which, following Van Bemmelen, we shall denominate micellian water. It is just as much a characteristic of the plastic or colloid condition as water of crystallization is a characteristic of many crystals, although just as we may have in certain cases crystal water replaced by alcohol or ether, etc., of crystallization, we can have the water in these colloids replaced by organic liquids, yielding alkogels, sulphogels, glycerogels, acetogels, etc. Further than this, all the recent work that has been done on the occlusion of solids by colloids points to the fact that water can be replaced by numbers of other substances. Even solids seem to be absorbed into the micellian structure, but this leads up to the question of solid solutions, a subject too large for discussion in the present paper.

Van Bemmelen has shown that this inhibited or micellian water differs from hygroscopic water in the ordinary sense of that word. Micellian water is absorbed into the structure of the particles of a powder of an inorganic hydrogel without changing the physical appearance, even under the microscope. Hygroscopic water is usually adsorbed on the particles, producing a distinct appearance of wetness. Heating does not usually destroy the hygroscopic qualities of a substance; it invariably destroys the absorptive power of the micellian structure, if pushed far enough.

It is not the purpose of this paper to review the work that has been done on colloids. A good bibliography of the whole subject has been given, up to 1901 by Whitney and Ober.<sup>1</sup> The immediate object is to call attention to certain significant qualities which are shared in common by such inorganic hydrogels as silicic acid, and ferric hydroxide on the one hand, and plastic clays and rock powders on the other. Both contain combined water; both lose water on heating, and take it up again on cooling in moist atmospheres (see curves in Fig. 1). Both gradually lose this

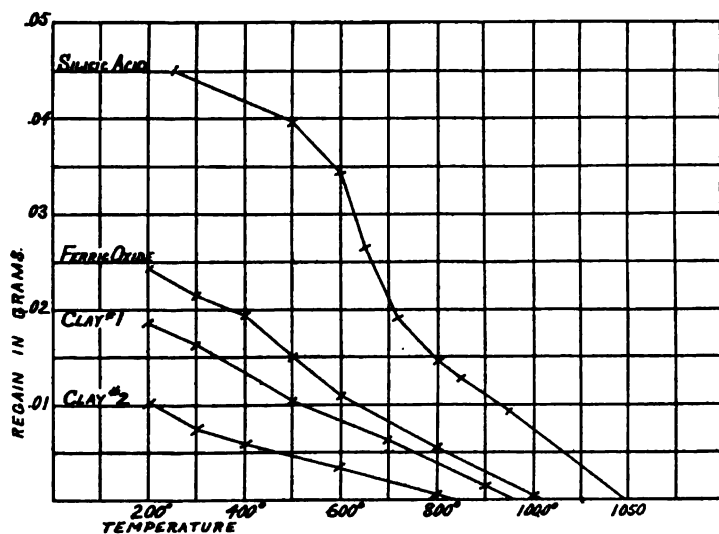


Fig. 1.

power on continued heating at high temperatures, and finally lose it entirely, together with plasticity, if the heating is pushed far enough. Very highly plastic clays and rock powders, after working up with water, usually shrink and deform on drying out; this quality is also universally noted in the case of the hydrogels. Silicic acid which has been air-dried can have water pressed out of it by subjecting it to very high pressures; the same phenomenon is known in the case of clays in the manufacture of hydraulic pressed brick. It has been frequently claimed that the cause of plasticity is to be sought in the aluminum silicate (kaolin) which forms the essential ingredient in all clays. The following is

<sup>1</sup> *Loc. cit.*

quoted from a late writer on the subject.<sup>1</sup> "Based on the work of various chemists, on that of investigators, using the microscope, with high powers, and on the physical experiments of Le Chatelier, it may now be said to have been established, that there are various hydrous silicates of aluminum, which differ in the proportion in which the elements are combined, and in form and structure, *some being colloid or amorphous* and others crystalline."

G. H. Cook,<sup>2</sup> a high authority on clays, writing in 1878 and describing his microscopical examinations, says: "Some clays appear to consist of well-defined crystalline forms; others show a few of these in a mass of fragmentary shapes; others still seem to be wholly made up of irregular forms and exceedingly fine particles of matter." Cook then calls attention to the fact that highly plastic clays are in the latter class and finally includes this very suggestive sentence; "We know that in some of the metals a tendency to crystallization reduces their tensile strength—most notably in the case of iron; and it may be that the crystalline structure of clay is somewhat analogous to the metals. Thus far there seems to be a close correspondence between this [non-crystalline] state or condition and the property of plasticity, and it appears to be a reasonable explanation consistent with most if not all the facts."

If indeed plasticity is a question of a colloid condition of the particles, it seemed that plastic clays and rock powders ought to show the same peculiar relation to water as is shown by the hydrogels, and in a diminishing degree as the plasticity diminishes.

In order to study the subject, a special form of furnace was devised that could be heated by a blast-lamp to any desired temperature up to 1100° C. The temperatures were measured by means of a Le Chatelier platinum-rhodium pyrometer. No difficulty was experienced in maintaining the temperatures constant to within a few degrees. The mode of procedure was as follows: Exact, 2 gram samples of the various substances were heated in the furnace for exactly one hour, cooled in a desiccator over concentrated sulphuric acid for one hour, weighed as quickly as possible and finally exposed under a large bell-jar over dilute sulphuric acid (24 per cent.) which had a vapor-pressure of about 18 mm. at 24° C.<sup>3</sup> At this vapor-pressure, water does not adsorb on the surface of

<sup>1</sup> Ladd: *Clay Record*, 18, 10.

<sup>2</sup> *Loc. cit.*, pp. 287, 288.

<sup>3</sup> Landolt and Börnstein: "Tabellen," Ed. 1894, p. 65.

glass or the particles of a powder so that all gains in weight are a true measure of affinity for water. As nearly as possible, the bell-jar was kept at a constant temperature during the experiments, but when any considerable variation occurred, corrections were made to the results. The silicic acid hydrogel was prepared by neutralizing sodium silicate with dilute hydrochloric acid, and washing the jelly by dialysis until the salt was entirely removed. The pure jelly was dried to a certain point on the steam-bath and finally allowed to air-dry. The resulting white powder, which had every physical appearance of being dry, was found to contain about 20 per cent. of water. The hydrogels of iron, alumina and magnesia were precipitated by dilute solutions of sodium hydroxide,

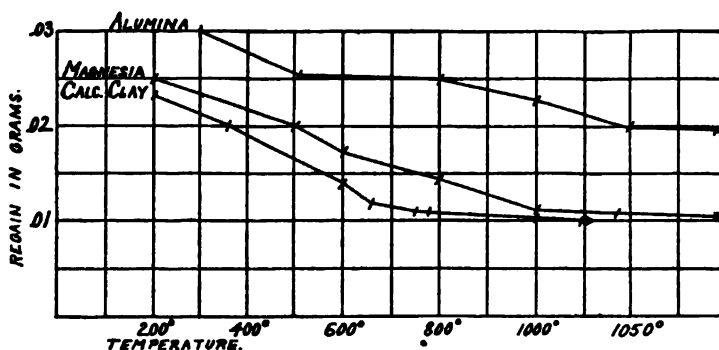


Fig. 2.

thoroughly washed by decantation and finally air-dried. Finally three samples of clay were selected for comparison. Clay No. 1 was highly plastic, clay No. 2 less so, and clay No. 3 contained an unusual amount of calcium carbonate. The results of the experiments are graphically shown in Figs. 1 and 2. On the horizontal axes, the temperatures of the heats in the furnace are shown, and on the vertical axes, the regain weights after one hour's exposure in the bell-jar. The curves of Fig. 1 indicate that identically the same peculiar power of absorbing water, which is gradually destroyed by heating, is possessed by clays and colloids. The difference is merely in degree. In Fig. 2 we have the curves for alumina and magnesia compared with that obtained from a calcareous clay of low fusing-point which contained 30.75 per cent. of calcium carbonate. These curves never descend to the zero-point. No amount of heating will destroy the power of lime, magnesia

and alumina to take up water again. Whatever theory we may hold as to the relation of water to these substances in the process of "slaking" it is quite certain that it is an altogether different phenomenon from the process which goes on when water is absorbed into the peculiar structure of a colloid. Table VI presents a series of observations made on a number of different samples in which the temperature of the heats was constant and the cementing values and the percentage of regain are the variables.

TABLE VI.

Sample No.	Name.	Cementing value.	Loss per cent. at 300.	Regain per cent. in air at 18 mm. V. L.
534	Clay	595	2.31	2.09
557	Clay	475	1.00	0.75
361	Clay limestone	158	0.40	0.40
335	Diabase	110	0.30	0.18
517	Diabase	76	0.43	0.43
566	Diabase	38	0.17	0.13
499	Quartzite	4	0.07	0.03
570	Gravel	2	0.08	0.04
468	Gneiss	1	0.04	0.00

The results are shown graphically in Fig. 3, the cementing

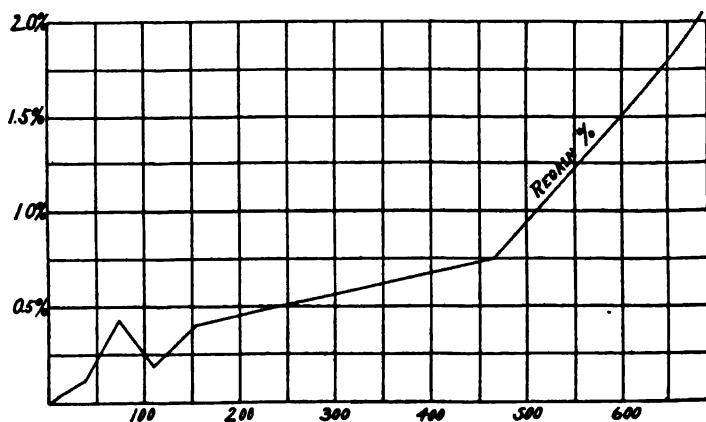


Fig. 3.

values being plotted on the horizontal, and the regain percentages on the vertical axis. The tendency of low regains to accompany low plasticity in these cases is undoubted, although the curve is by no means regular. Good reasons for irregularities are not hard to find; in the first place, impact testing, though it may be the

best, is not a perfect measure of cementing value and is subject to considerable error. In the second place, it is freely admitted that other influences such as shape and size of particles, solubility of ingredients, the ratio of plastic to non-plastic material present, etc., may come into play.

A question that naturally arises is how are we to account for the well-known high-binding powers of many homogeneous crystalline rocks such as limestones and dolomites. Reference to Table IV shows a wide range in cementing value for this class of material. As a matter of fact, pure calcium carbonate has no cementing value whatsoever; this quality is provided by certain hydrated impurities such as silica, ferric oxide or even clay. The amount of these impurities need not necessarily be very large, but the distribution throughout the mass is probably of a very intimate nature. It has long been known to practical road builders that the binding power of many rocks increases as time goes on, under the combined influence of the action of traffic and water. Every potter knows that the plasticity of clay increases under the action of kneading and working with water. In some industries, clay mixtures are stored away for considerable periods under wet blankets. This process is called "sweating" and is believed to be very beneficial. It has lately been suggested that bacterial fermentations are responsible for the improvement in the quality of clays under such treatment. The writer has no data on this subject but it is well known that many of the nitrifying bacteria flourish in media composed of inorganic colloids, which suggests that the presence of bacteria may be a concomitant rather than the cause of improvement. Experiments in the laboratory have shown that the cementing value of briquettes is increased, if the dough made from a rock dust is allowed to stand for some time before being molded, and it is still more increased, if the dough is kneaded. This is plainly shown by the results of a sample of dolomite that had an analysis as follows:  $\text{CaCO}_3$ , 54.30;  $\text{MgCO}_3$ , 36.20; combined water, 0.48; silica, 3.00; iron and alumina, etc., 7.00. This dolomite is a celebrated road-building material in the locality in which it is found and its most marked characteristic is the way that its binding power increases after it has been upon the road for some time. In the following table, the rock dust was mixed with water and briquettes made at separate intervals; finally a new lot

of dust was made to a dough and well kneaded by hand for one hour.

TABLE VII.

	Time.	Cementing value.
At once		16
Dough	4 hours old	50
"	24 " "	81
"	72 " "	79
"	96 " "	77
"	120 " "	79
"	144 " "	83
"	8 days	81
"	kneaded 1 hour	190

In summarizing the results as presented in this paper it may be said that it has been pointed out: (1) That the cementing power of rock powders is a property similar to the plasticity of clays. (2) That all rock powders that have cementing power show the same peculiar relation to water that is shown by substances that possess an amorphous colloid structure, *i. e.*, they can be dehydrated and rehydrated, until, by prolonged high heating, the structure is destroyed.

It is not the intention of the writer to maintain that the gelatinous mass in which silicic acid separates from a dilute solution is in any way comparable to a plastic clay mass. The question is purely one of the condition of the particles which go to make up the mass of plastic rock-powder or clay. In the opinion of the writer, particles which are entirely crystalline in their nature have nothing to do with plasticity except to act as a diluent. It is the amorphous particles which, by reason of their characteristic structure, are able to absorb water and assume the condition which causes them to exhibit that coherence which in the mass we denominate plasticity.

A series of clays which is at present being studied in this laboratory according to the methods already described for obtaining the curves of Fig. 1, has given results which go to show that the more plastic a clay the more it exhibits the peculiar absorptive power. Before publishing the results, it will be necessary, however, to collect evidence from a great number of different kinds of clays. To that end the writer will be grateful to any one who will send samples to this laboratory for comparison and study.



## THE SOLUBILITY OF THE CHLORIDE, THE BROMIDE, AND THE IODIDE OF LEAD, IN WATER, AT TEMPERATURES FROM 0° UPWARD.

BY D. M. LICHTY.

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THE solubility of lead chloride at 25°, as given by von Ende,<sup>1</sup> is 38.8 milligram-molecules or 10.678 grams per liter of solution, and therefore somewhat higher in 1000 grams of water. Ditte<sup>2</sup> gives the solubility in 1000 grams of water as 8 grams at 0°, 11.8 at 20°, 17 at 40°, 21 at 55°, and 31 at 80°. The solubility was found to be higher at 20° than von Ende found it at 25°. According to Bell,<sup>3</sup> the solubility at 16.5° is 9.503 grams<sup>4</sup> in 1000 of water, while the solubility at the same temperature based on Ditte's results is about 11 grams in 1000 of water. The data on the solubility of the bromide and the iodide being even less satisfactory, the writer undertook to determine the solubility of these three salts at different temperatures from 0° upward. The purity of the salts used is attested by the results of analysis given later. Very pure water, such as is used in electric conductivity work, was employed.

The saturated solutions were prepared by making approximately saturated solutions at a higher temperature (generally by 10°) than the one at which the solubility was to be determined, and then placing these solutions in a bath at the desired temperature for about six hours. The considerable quantity of larger crystals which always formed over the smaller crystals left undissolved in the bottom of the flask, served to show that the solutions had really been supersaturated with respect to the temperature of measurement. The flasks used for making the solutions had a capacity of 250 cc. and were immersed to the lip in the bath and stoppered. From these, calibrated glass-stoppered flasks (capacity 100 cc.) which were brought to the working temperature by weighing and immersing in the bath, were filled to a point slightly above the mark by means of a siphon and rubber bulb. After a few minutes,

<sup>1</sup> *Ztschr. anorg. Chem.*, 26, 134 (1901).

<sup>2</sup> *Compt. Rend.*, 92, 718.

<sup>3</sup> *Chem. News*, 16, 69.

<sup>4</sup> A saturated solution of lead chloride contains 0.9414 per cent. of the salt at 16.5°, is the substance of Bell's statement.

the solutions were carefully brought to the mark by means of a pipette. The flasks and their contents were then rapidly brought to the temperature of the room, dried and weighed, after which the solutions were transferred to weighed platinum dishes, evaporated and then dried at  $180^{\circ}$  for several hours. The evaporation proved very tedious, owing to the fact that on the surface of the solutions there collected a very thin film of crystals through which burst gas bubbles rising from the bottom of the dishes, thus causing a small amount of the salt to be thrown out, which could be prevented only by very frequent stirring until the solutions were from one-half to three-fourths evaporated.

The measuring flasks were calibrated either at  $20^{\circ}$  or  $25^{\circ}$ , and at all other temperatures corrections were made for either expansion or contraction. Each weight of solution was reduced to weight *in vacuo*, while the weight of the salt was not, the correction amounting at most to only 0.2 milligram. The data were reduced to solubility in grams and milligram-molecules per liter of solution and to grams and milligram-molecules per 100 grams of water. The densities compared with water at  $4^{\circ}$  C. were also calculated.

The flasks chosen for measuring the solutions had necks of such diameter that a length of 10 mm. had a capacity of about 0.6 gram of water at  $25^{\circ}$  or 6 milligrams per 0.1 mm., so that the meniscus could be adjusted to  $\pm 10$  milligrams or 1 part in 10,000 for water, and to a but slightly larger quantity for the solutions, whose densities did not differ much from the density of water.

Below  $45^{\circ}$  the temperatures were maintained within less than  $0.1^{\circ}$ , for  $45^{\circ}$  and  $55^{\circ}$  to about  $0.1^{\circ}$ , for  $65^{\circ}$  and  $80^{\circ}$  within  $0.2^{\circ}$ , and for  $95^{\circ}$  within  $0.3^{\circ}$ , the correct temperature being determined by means of a standardized instrument, whose  $0^{\circ}$  and  $100^{\circ}$  points had not measurably altered since the standardizing.

#### ANALYSIS OF SALTS.

	Gram.
Lead chloride taken.....	0.3848
Silver chloride obtained .....	0.3970
Silver chloride calculated.....	0.3971
Lead bromide taken.....	0.4468
Silver bromide obtained .....	0.4572
Silver bromide calculated.....	0.4576
Lead iodide taken.....	0.2462
Silver iodide obtained.....	0.2507
Silver iodide calculated.....	0.2510

TABLE I.—SOLUBILITY OF LEAD CHLORIDE IN MILLIGRAM-MOLECULES.

Temperature.	Milligram-molecule per 100 cc. solution.		Milligram-molecule per 100 grams water.		Density referred to water at 0°.	
0°	2.428	....	2.428	....	1.00666	....
0°	2.415	2.421	2.415	2.421	1.00665	1.00665
15°	3.266	....	3.273	....	1.00695	....
15°	3.264	3.265	3.271	3.272	1.00691	1.00693
25°	3.878	....	3.905	....	1.00726	....
25°	3.887	3.882 <sup>1</sup>	3.901	3.903	1.00724	1.00725
35°	4.734	....	4.768	....	1.00602	....
35°	4.732	4.733	4.766	4.767	1.00598	1.00600
45°	5.580	....	5.646	....	1.00417	....
45°	5.578	5.579	5.642	5.644	1.00429	1.00423
55°	6.484	....	6.553	....	1.00206	....
55°	6.488	6.486	6.594	6.573	1.00195	1.00200
65°	7.498	....	7.655	....	0.99938	....
65°	7.482	7.490	7.647	7.651	0.99928	0.99933
80°	9.149	....	9.439	....	0.99465	....
80°	9.152	9.150	9.440	9.439	0.99484	0.99474
95°	10.931	....	11.395	....	0.98962	....
95°	10.922	10.926	11.393	11.394	0.98921	0.98941
100° <sup>2</sup>	....	11.52	....	12.01	....	....

TABLE II.—SOLUBILITY OF LEAD BROMIDE IN MILLIGRAM-MOLECULES.

Temperature.	Milligram-molecule per 100 cc. of solution.		Milligram-molecule per 100 grams of water.		Density referred to water at 0°.	
0°	1.242	....	1.242	....	1.00435	....
0°	1.241	1.241	1.241	1.241	1.00431	1.00433
15°	1.990	....	1.991	....	1.00525	....
15°	1.985	1.987	1.988	1.989	1.00536	1.00530
25°	2.648	....	2.658	....	1.00617	....
25°	2.644	2.646 <sup>3</sup>	2.652	2.655	1.00599	1.00608
35°	3.589	....	3.615	....	1.00587	....
35°	3.566	3.577	3.592	3.603	1.00609	1.00598
45°	4.704	....	4.758	....	1.00601	....
45°	4.706	4.705	4.763	4.760	1.00586	1.00593
55°	5.743	....	5.840	....	1.00449	....
55°	5.719	5.731	5.814	5.827	1.00461	1.00455
65°	6.870	....	7.027	....	1.00284	....
65°	6.849	6.859	7.006	7.016	1.00281	1.00282
80°	8.812	....	9.107	....	1.00000	....
80°	8.826	8.819	9.120	9.113	1.00007	1.00003
95°	11.387	....	11.890	....	0.99948	....
95°	11.386	11.386	11.890	11.890	0.99945	0.99946
100° <sup>4</sup>	....	12.40	....	12.94	....	....

<sup>1</sup> Von Ende, 38.8 per liter.

<sup>2</sup> By extrapolation, see Fig. 1.

<sup>3</sup> Von Ende, 26.26 per liter.

<sup>4</sup> By extrapolation, see Fig. 1.

TABLE III.—SOLUBILITY OF LEAD IODIDE IN MILLIGRAM-MOLECULES.

Temperature.	Milligram-molecule per 100 cc. of solution.		Milligram-molecule per 100 grams of water.		Density referred to water at 0°.	
0°	0.096	....	0.096	....	1.00057	....
0°	0.096	0.096	0.096	0.096	1.00055	1.00056
15°	0.132	....	0.132	....	0.99982	....
15°	0.134	0.133	0.134	0.133	0.99984	0.99983
25°	0.166	....	0.166	....	0.99801	....
25°	0.165	0.165 <sup>1</sup>	0.165	0.166	0.99795	0.99798
35°	0.224	....	0.225	....	0.99498	....
35°	0.225	0.224	0.227	0.226	0.99518	0.99508
45°	0.313	....	0.316	....	0.99158	....
45°	0.312	0.312	0.315	0.315	0.99149	0.99153
55°	0.374	....	0.380	....	0.98729	....
55°	0.374	0.374	0.382	0.381	0.98717	0.98723
65°	0.465	....	0.474	....	0.98264	....
65°	0.464	0.464	0.473	0.473	0.98272	0.98268
80°	0.636	....	0.655	....	0.97450	....
80°	0.639	0.637	0.657	0.656	0.97454	0.97452
95°	0.829	....	0.860	....	0.96689	....
95°	0.827	0.828	0.858	0.859	0.96730	0.96709
100° <sup>2</sup>	....	0.895	....	0.927	....	....

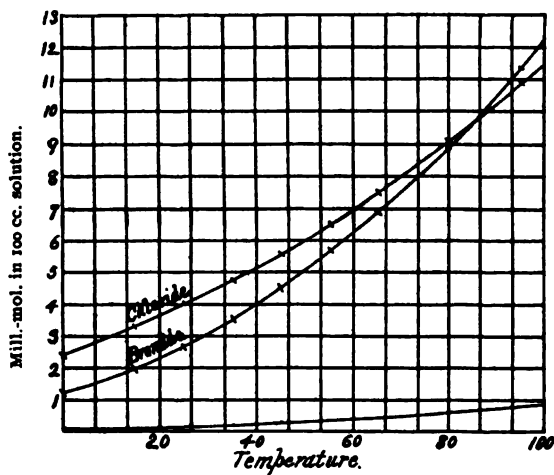


Fig. 1.

A comparison of the data in the three foregoing tables will at once show that the solubility curves based on milligram-molecules in 100 cc. of solution and those based on milligram-molecules in 100 grams of water will be similar, the latter turning a little far-

<sup>1</sup> Von Ende, 1.59 per liter.

<sup>2</sup> By extrapolation, see Fig. 1.

ther away from the temperature axis than the former; it was consequently deemed sufficient to draw the curves for the former. Either the data or the curves show that at the lower temperatures the molecular solubility of the bromide is less than that of the chloride, but that the solubility of the former increases more rapidly with the temperature than does that of the latter, and that the solubilities are the same between  $80^{\circ}$  and  $95^{\circ}$ . The curves show that the temperature of common solubility is  $88.5^{\circ}$  and the solubility 10.15 milligram-molecules. The solubility of the iodide is decidedly less than that of either of the other salts, not reaching, even at  $100^{\circ}$ , the same value as that of the bromide at  $0^{\circ}$ .

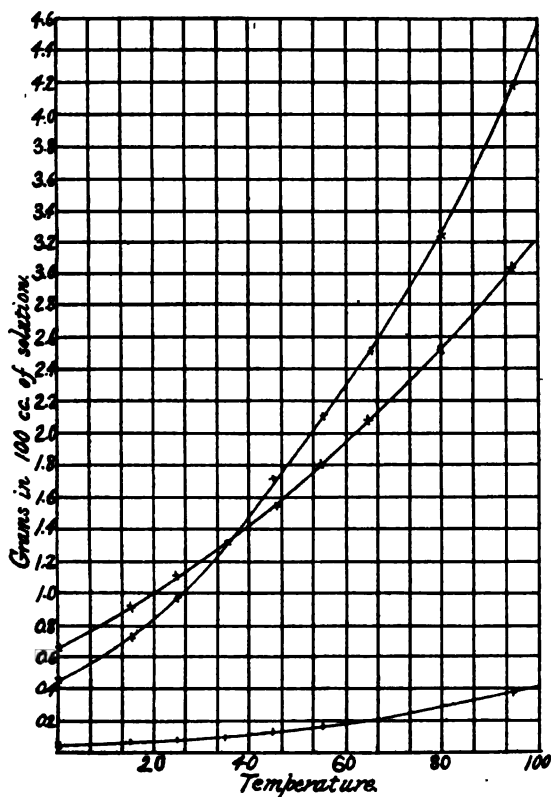


Fig. 2.

TABLE IV.—SOLUBILITY BY WEIGHT.

Temperature.	Chloride.		Bromide.		Iodide.	
	Grams in 100 cc. solution.	Grams in 100 grams water.	Grams in 100 cc. solution.	Grams in 100 grams water.	Grams in 100 cc. solution.	Grams in 100 grams water.
0°	0.6728	0.6728	0.4554	0.4554	0.0442	0.0442
15°	0.9070	0.9090	0.7285	0.7305	0.0613	0.0613
25°	1.0786	1.0842	0.9701	0.9744	0.0762	0.0764
35°	1.315	1.3244	1.3124	1.3220	0.1035	0.1042
45°	1.5498	1.5673	1.7259	1.7457	0.1440	0.1453
55°	1.8019	1.8263	2.1024	2.1376	0.1726	0.1755
65°	2.0810	2.1265	2.5161	2.5736	0.2140	0.2183
80°	2.5420	2.6224	3.2350	3.3430	0.2937	0.3023
95°	3.0358	3.1654	4.1767	4.3613	0.3814	0.3960
100° <sup>1</sup>	3.208	3.342	4.550	4.751	0.420	0.436

At 0° the solubility of the chloride by weight is about one and one-half times that of the bromide; at 35°, their solubilities are practically equal and at 95° that of the chloride is about three-fourths of that of the bromide.

DEPARTMENT OF GENERAL CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH., March, 1903.

## THE CARBOHYDRATE GROUP IN THE PROTEIN MOLECULE.<sup>1</sup>

BY THOMAS B. OSBORNE AND ISAAC F. HARRIS.

Received February 25, 1903.

IT HAS been known for some time that certain complex substances found in animal organisms, when decomposed with acids, yielded protein and carbohydrate bodies, together with other products. These substances, known as mucins, mucoids, chondroproteids, nucleins, hyalogen substances, etc., are generally regarded as compounds in which the protein is united with some other complex organic group of which this carbohydrate is a part. Although several investigators long ago suggested the possible presence of a carbohydrate group in the protein molecule proper, no evidence of weight supported this view until Pavy,<sup>2</sup> by hydrolyzing coagulated ovalbumin, obtained a solution from which he prepared an osazone with a melting-point near that of glucosazone. In consequence of this discovery, Pavy concluded that his investigations brought "the extensive group of proteids of both the animal and vegetable kingdoms of nature into the class of glucosides."

This announcement of Pavy's led to numerous investigations

<sup>1</sup> By extrapolation, see Fig. 2.

<sup>2</sup> From the laboratory of the Connecticut Agricultural Experiment Station.

<sup>3</sup> "Physiology of the Carbohydrates."

followed by many contradictory statements respecting the presence of the carbohydrate group in the protein molecule proper. It has, however, been definitely proved that several of the animal proteins which are not, at present, considered to be compounds of protein with non-protein substances, yield carbohydrate which has been identified with chitosamine, conalbumin, the globulins of egg white and of egg yolk. Chitosamine has been obtained from crystallized ovalbumin, serum albumin, and an osazone from the mixed globulins of the blood serum. From no other "simple" protein, so far as we can find, is it certain that carbohydrate has been directly obtained.

The presence of a carbohydrate group in the protein molecule is, however, generally assumed, because it is commonly supposed that all proteins, casein excepted, give Molisch's reaction. This is a furfural reaction of great delicacy and is given by minute quantities of all carbohydrates when decomposed with strong sulphuric acid, even though they, like the hexoses, yield but a small proportion of furfural. As Molisch's reaction has been applied to only a few of the vegetable proteins, we have tested a series of them in order to see if they, like the animal proteins, would all give this reaction.

We have also attempted to determine quantitatively the amount of furfural which these proteins yield, by boiling them with hydrochloric acid (sp. gr. 1.06), collecting the distillate and precipitating with phloroglucin in the usual way. The aniline acetate test was also applied to the distillate, in order to detect any minute quantities of furfural which it might contain. The results of these experiments are given in the following table, in which the proteins are arranged as far as possible in the order of the intensity of the Molisch reaction which they gave under practically the same conditions, which were the following:

Ten milligrams of the protein were suspended in 1 cc. of water, 2 drops of a 15 per cent. alcoholic solution of  $\alpha$ -naphthol were added, and then 3 cc. of concentrated sulphuric acid.

This method yields only approximately comparative results but is sufficient to show, in a general way, the relative intensity of the reaction.

Those proteins which gave no Molisch reaction were also tested in larger quantity, but with perfectly negative results.

The outcome of these experiments was as follows:

## FURFURAL REACTIONS GIVEN BY VARIOUS PROTEINS.

Protein.	Condition.	Source.	Molisch reaction.	Anilise acetate.	Phloroglucin.
Avenalin.	Crystals.	Oatseed.	None.	....	....
Edestin.	Crystals.	Hempseed.	None.	None.	None.
Globulin.	Crystals.	Castor-bean.	None.	....	....
Casein.	Amorphous.	Cow's milk.	None.	....	....
Globulin.	Crystals.	Flaxseed.	Trace.	None.	None.
Legumin.	Spheroids.	Vetch.	Slight.	None.	....
Legumelin.	Amorphous.	Cow-pea.	Slight.	....	....
Zein.	Amorphous.	Maize.	Slight.	None.	None.
Legumin.	Spheroids.	Horse-bean.	Slight.	None.	....
Amandin.	Spheroids.	Almonds.	Slight.	None.	None.
Globulin.	Spheroids.	Sunflower.	Slight.	None.	None.
Glycinin.	Spheroids.	Soy bean.	Slight.	None.	None.
Excelsin.	Crystals.	Brazil-nut.	Slight.	None.	None.
Legumin.	Spheroids.	Lentil.	Slight.	None.	None.
Globulin.	Spheroids.	Cottonseed.	Moderate.	None.	None.
Glutenin.	Amorphous.	Wheat flour.	Moderate.	....	....
Hordain.	Amorphous.	Barley flour.	Strong.	None.	None.
Ovalbumin.	Crystals.	Hen's egg.	Strong.	Slight trace.	Slight trace.
Gliadin.	Amorphous.	Wheat flour.	Strong.	None.	None.
Vignin.	Spheroids.	Cow-pea.	Strong.	None.	None.
Nucleovitelin.	Amorphous.	Hen's egg.	Strong.	None.	None.
Leucoscin.	Amorphous.	Wheat flour.	Very strong.	....	....
Phaseolin.	Spheroids.	Adzuki bean.	Very strong.	None.	None.
Phaseolin.	Crystals.	Kidney bean.	Very strong.	....	....



It is to be noted that several of these proteins gave no reaction whatever<sup>1</sup> and therefore contain no carbohydrate; that a larger number gave only a slight reaction, which, in view of the great delicacy of Molisch's test, must be attributed to a slight contamination of the preparation with some carbohydrate; that the rest gave positive reactions, some even stronger than was given by ovalbumin, which is known to contain a considerable amount of carbohydrate. From this we conclude that these latter may possibly contain a carbohydrate group. None of the proteins yielded any furfural when boiled with hydrochloric acid, except ovalbumin, which showed a trace, and none of these, therefore, contain a measurable proportion of any pentose-yielding group. After these tests had been made, Grund<sup>2</sup> published the results of similar attempts to obtain furfural from animal proteins, but with the same negative results. Whether those proteins which do not yield an osazone but which give a strong Molisch reaction actually contain a carbohydrate group cannot thus be determined. Molisch's reaction is of such extreme delicacy that mere traces of carbohydrate are sufficient to cause a strong reaction, especially if these, like the pentoses and nucleic acids, yield large proportions of furfural when hydrolyzed by acids.

In order to determine the intensity of this reaction with small quantities of carbohydrates, we tried the following experiments:

*Cellulose*.—0.5 milligram of filter-paper gives a very powerful reaction, much more intense than was given by any of the proteins tested.

*Hexose*.—0.1 milligram of dextrose gave as strong a reaction as those marked strong in the table.

*Pentose*.—0.1 milligram of arabinose gave a strong reaction; 0.05 milligram a decided one.

*Furfural*.—0.01 milligram gave a strong pink.

*Nucleic Acid*.—0.5 milligram of nucleic acid gave a strong reaction, while 0.05 milligram gave one similar to those given by the proteins marked slight. 0.5 milligram of nucleic acid would correspond to a phosphorus content of 0.5 per cent., 0.05 milligram to 0.05 per cent. of the quantity of protein used in these tests—a quantity which would be readily detected. From these experiments it is evident that very small quantities of contaminating

<sup>1</sup> Erb (*Ztschr. Biol.*, 41, 309) has stated that edestin does not give Molisch's reaction.

<sup>2</sup> *Ztschr. physiol. Chem.*, 38, 111 (1902).

substances, many or all of which are liable to be present with the protein, especially in vegetable extracts, may be quite enough to cause a strong Molisch reaction.

The evidence of a carbohydrate group in the protein molecule which Molisch's reaction affords cannot, therefore, be accepted as conclusive, other evidence which shows that more than insignificant quantities of carbohydrate are present being also necessary.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 77.]

***p*-AMINOBENZONITRILE.<sup>1</sup>**

BY MARSTON TAYLOR BOGERT AND LOTHAIR KOHNSTAMM.

Received March 9, 1903.

INTRODUCTORY.

IN the last edition of Beilstein's "Handbuch," Vol. II, p. 1273, three widely separated melting-points are recorded for *p*-aminobenzonitrile, namely, 74°, as reported by Engler;<sup>2</sup> 110°, reported by Fricke;<sup>3</sup> and 86°, reported by Griess.<sup>4</sup> In the recent German edition of "Roscoe and Schorlemmer," and in Richter's "Lexikon," the preference is given to the figure 110°—why, we do not know, unless it is due to the usual inclination on the part of compilers of reference works to give the preference to the highest figure. As the matter is not cleared up in the recently issued supplement to "Beilstein" (Vol. II), and as we have not been able to discover anything in the literature which would further enlighten us, it seemed of interest to investigate the subject, and to determine if possible which of these widely divergent melting-points (if any, indeed, were correct) represented the real melting-point of *p*-aminobenzonitrile, especially as a further study of this nitrile and its derivatives was contemplated.

The results obtained show quite clearly that the melting-point of 86°, as given by Griess,<sup>5</sup> is substantially correct. We have repeated the work of Engler, Fricke and Griess, and have also prepared the nitrile by a fourth method. The products obtained

<sup>1</sup> Read before the New York Section at its meeting May 20, 1902.

<sup>2</sup> *Ztschr. Chem.* (1868), p. 613; *Ann. Chem.* (Liebig), 149, 297 (1869).

<sup>3</sup> *Ber. d. chem. Ges.*, 7, 1321 (1874).

<sup>4</sup> *Ibid.*, 8, 861 (1875).

<sup>5</sup> *Loc. cit.*

by the various methods were identical in all respects, and melted sharply at 85.5°-86° (corr.). A few derivatives of the aminonitrile were also prepared.

## EXPERIMENTAL.

*p*-Nitrobenzonitrile.—This was prepared from *p*-nitraniline by the Sandmeyer reaction, in a manner entirely analogous to that already described by Bogert and Hand<sup>1</sup> for the ortho compound, carbon tetrachloride being used to extract the crude nitrile from the accompanying mineral cyanides, and further purification being accomplished by crystallization from dilute acetic acid. The crystals thus obtained melted sharply at 147° (uncorr.). Fricke<sup>2</sup> and Hantzsch and Schultze<sup>3</sup> give the melting-point as 147°, while Sandmeyer<sup>4</sup> reports it as 146°. It will be noted that the melting-point of this nitrile is the same as that of the *p*-nitraniline from which it was prepared. We did not find the yield of nitrile to be nearly so large as in the case of the ortho compound. This is perhaps due to the formation of diazoamino<sup>5</sup> and biphenyl<sup>6</sup> compounds. The method recommended by Pinnow and Müller<sup>7</sup> was also tried, but the yield was still less satisfactory. By the action of concentrated sulphuric acid, this nitrile may be changed to *p*-nitrobenzamide, melting-point 200° (uncorr.), as already observed by Claus.<sup>8</sup>

*Reduction of p*-Nitrobenzonitrile by Engler's Method.—Five grams of *p*-nitrobenzonitrile were dissolved in 100 cc. absolute alcohol, 12 cc. hydrochloric acid (sp. gr. 1.2) added, and the reduction accomplished by the use of 8 grams of granulated zinc, the mixture being allowed to stand for two days with frequent shaking. It was then filtered and the alcohol removed from the filtrate by distillation under diminished pressure. From the residual solution, on cooling, there separated a mass of fine needles, which were washed thoroughly with cold water (to remove zinc salts) and added to a mixture of cracked ice and ether

<sup>1</sup> This Journal, 24, 1035 (1902).

<sup>2</sup> *Loc. cit*

<sup>3</sup> *Ber. d. chem. Ges.*, 28, 666 (1895).

<sup>4</sup> *Ibid.*, 18, 1492 (1885).

<sup>5</sup> Schraube and Schmidt: *Ber. d. chem. Ges.*, 27, 520 (1894).

<sup>6</sup> Niementowski: *Ibid.*, 34, 3325 (1901).

<sup>7</sup> *Ibid.*, 28, 149 (1895).

<sup>8</sup> *J. prakt. Chem.* (2), 81, 399 (1895).

in a separatory funnel. Caustic alkali was then run in to alkaline reaction and the solution repeatedly extracted with ether. The ether extracts were combined, the ether distilled off, and the liquid residue placed over sulphuric acid *in vacuo*, where it soon solidified in a crystalline mass. On recrystallization from water, long white needles were obtained, melting-point  $85.5^{\circ}$ - $86^{\circ}$ .

Engler gives the melting-point of his product as  $74^{\circ}$ , and it is, therefore, quite evident that his material could not have been pure *p*-aminobenzonitrile. In his purification of the crude aminonitrile he evaporated the alkaline solution of the free base until an oil separated upon the surface which solidified on cooling, and then recrystallized this until it showed a melting-point of  $74^{\circ}$ . That some saponification occurred in this evaporation of the alkaline solution seems more than likely, and Engler admits that the mother-liquors contained the sodium salt of what was apparently *p*-aminobenzoic acid. His product was probably a mixture, in spite of the fact that the percentage composition as ascertained by analysis corresponded with that calculated for *p*-aminobenzonitrile.

*Reduction of p-Nitrobenzonitrile by Fricke's Method.*—We have found it more convenient, in carrying out this process, to use alcohol, although Fricke does not mention this in his description of the method. Five grams of the nitronitrile were dissolved in 100 cc. of absolute alcohol and reduced with 10 cc. of glacial acetic acid and 10 grams of granulated tin, adding a few drops of platonic chloride to start the reaction. Several days were required for complete reduction. The tin was then precipitated by hydrogen sulphide, the filtrate neutralized with sodium carbonate and evaporated to dryness, the residue extracted with ether, and the ethereal extracts evaporated *in vacuo*. The crystals thus obtained were recrystallized from water, then appearing as long white needles, melting-point  $85.5^{\circ}$ - $86^{\circ}$ , and identical with the reduction-product from Engler's method. Fricke reports the melting-point of his product as  $110^{\circ}$ . From his method of purifying the crude material (which is not given in the article quoted, but appears in his dissertation)<sup>1</sup> it is difficult to determine the particular compound or mixture which he had in hand. It seems manifest, however, that his product was not pure *p*-aminobenzonitrile as he believed.

<sup>1</sup> Inaugural Dissertation Göttingen, 1874, "Ueber Nitro- und Amido-Benzonitrile."

*Preparation of p-aminobenzonitrile by Griess's Method.*—Twenty grams of *p*-uraminobenzoic acid was distilled with phosphorus pentoxide, and the impure *p*-aminobenzonitrile thus produced was purified by recrystallization from water, until the melting-point remained constant at 85.5°-86°, the purified substance being identical in all respects with the *p*-aminobenzonitrile already described. Our results, therefore, agree entirely with those of Griess.

*Reduction of p-Nitrobenzonitrile by Stannous Chloride and Hydrochloric Acid.*—The reduction of the nitronitrile in this case was carried out exactly as outlined by Bogert and Hand<sup>1</sup> for the ortho compound. The crude aminonitrile, crystallized from water, formed long white needles, melting at 85.5°-86°, and identical with the *p*-aminobenzonitrile obtained by the other methods. In this reduction, care must be taken to make sure that the reaction is complete, as the tendency to separate intermediate reduction products (azoxy-, hydroxylamino-derivatives, etc.) appears to be greater than with the orthonitronitrile.

Some of the pure material, obtained by this latter method, was analyzed with the following results:

		Found.				
Calculated for C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> .		I.	II.	III.	IV.	V.
Carbon.....	71.18	71.11	71.33	....	....	....
Hydrogen .....	5.09	5.19	5.18	....	....	....
Nitrogen .....	23.72	....	....	23.88	23.53	23.70

*Properties of p-Aminobenzonitrile.*—Long white or colorless prisms, or compact glassy tablets. Large crystals may be obtained from a mixture of chloroform and petroleum ether, by careful evaporation. The melting-point is 85.5°-86° (corr.), and is not changed by further crystallization. It is very difficultly soluble in petroleum solvents, cold or hot; difficultly soluble in cold water, moderately soluble in hot; difficultly soluble in cold carbon bisulphide or carbon tetrachloride, slightly soluble in the same at their boiling-points; apparently insoluble in cold oil of turpentine, but dissolves readily on boiling; very easily soluble in methyl alcohol, ethyl alcohol, isoamyl alcohol, ether, ethyl acetate, ethyl nitrate, benzene, chloroform, acetone, or glacial acetic acid; apparently insoluble in concentrated hydrochloric acid, difficultly soluble in

<sup>1</sup> *Loc. cit.*

dilute; unattacked by cold concentrated caustic soda, but decomposed by it on boiling.

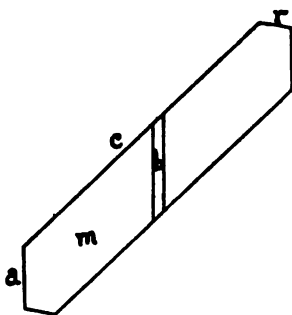
Through the kindness of Dr. Austin Flint Rogers, of the Department of Mineralogy of Columbia University, the following crystallographic data are appended:

Monoclinic system.  $a:b:c = 1.7475:1:1.4573$ .  $\beta = 47^\circ 50'$ .

Forms:  $a$  (100),  $b$  (010),  $c$  (001),  $m$  (110),  $r$  ( $\bar{1}01$ ).

		Observed.	Calculated.
$mm'$	(110 : $\bar{1}10$ ) (6)	$75^\circ 20'$	....
$ac$	(100 : 001) (6)	$47^\circ 50'$	....
$cr$	(001 : $\bar{1}01$ ) (3)	$54^\circ 32'$	....
$am$	(100 : 110) (8)	$52^\circ 24'$	$52^\circ 20'$
$cm$	(001 : 110) (6)	$65^\circ 42'$	$65^\circ 47'$

Crystals rhomboidal in shape, tabular parallel to  $c$ ; often quite elongate in the direction of the  $b$  axis. Faces  $c$  and  $m$  dominant;  $a$ ,  $b$  and  $r$ , subordinate, the two latter faces usually rounded.



Cleavage  $a$  perfect,  $b$  less so. The figure given above is an orthographic projection, with (010) as the plane of projection.

*Chloride of p-Aminobenzonitrile.*—This was prepared by dissolving the nitrile in dry ether and passing in dry hydrochloric acid gas. It separated immediately as a white crystalline precipitate. The determination of hydrochloric acid in this salt invariably gave low results, even when freshly precipitated, washed with absolute ether, and dried *in vacuo* over sulphuric acid.

*p-Acetaminobenzonitrile.*—The aminonitrile was boiled with acetic anhydride for a few hours and the crude product crystallized from water. Fine white needles, melting-point  $200^\circ$ . Percentage of nitrogen found by analysis, 17.52; required for  $\text{CH}_3\text{CONHC}_6\text{H}_4\text{CN}$ , 17.50.

*p*-Propionaminobenzonitrile.—This was prepared by heating the aminonitrile for several hours with propionic anhydride, and crystallizing the crude product from water. It forms crystals melting at 169°. Percentage of nitrogen found by analysis, 16.09; calculated for  $C_9H_9CONHC_2H_5CN$ , 16.06.

*p*-Aminobenzamide.—The aminonitrile was warmed for some time at 50° with alkaline hydrogen dioxide solution. On cooling, white crystals separated, melting-point 178°–179°. Not sufficient of the material was prepared for further purification, so that the melting-point as given is probably low. Reichenbach and Beilstein<sup>1</sup> report the melting-point of *p*-aminobenzamide as 178°–179°, but Remsen and Reed<sup>2</sup> give the corrected melting-point as 182.9°.

*p*-Aminobenzthiamide,  $H_2NCSC_6H_4CN$ .—The aminonitrile was dissolved in alcohol, the solution saturated at 0° with dry ammonia and dry hydrogen sulphide, and then heated in a sealed tube at 100° for several hours. The crystals obtained, when purified and dried, showed a melting-point of 172°. Engler<sup>3</sup> gives the melting-point of *p*-aminobenzthiamide as 170°.

The study of *p*-aminobenzonitrile and of its derivatives is being continued.

ORGANIC LABORATORY, HAVEMEYER HALL, COLUMBIA  
UNIVERSITY, March, 1903.

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE MOLECULAR REARRANGEMENT OF THIOCYAN-  
ACETANILIDES INTO LABILE PSEUDOTHIOHY-  
DANTOINS; AND ON THE MOLECULAR  
REARRANGEMENT OF THE LAT-  
TER INTO STABLE  
ISOMERS.

BY TREAT BALDWIN JOHNSON.

Received March 1, 1903.

[SECOND PAPER.]

In a previous paper from this laboratory by Wheeler and Johnson,<sup>4</sup> it was shown that a thiocyanacetanilide is capable of a

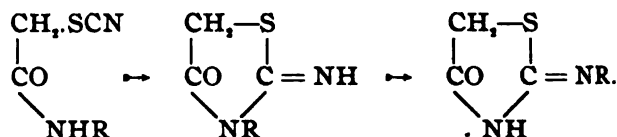
<sup>1</sup> *Ann. Chem. (Liebig)*, 132, 137 (1864).

<sup>2</sup> *Am. Chem. J.*, 21, 281 (1899).

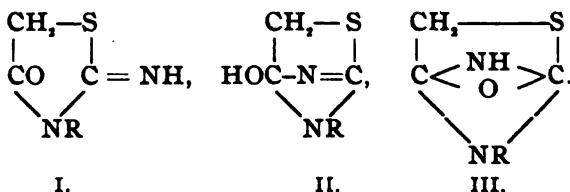
<sup>3</sup> *Ztschr. phys. Chem.*, 1868, p. 613; *Ann. Chem. (Liebig)*, 149, 297 (1869).

<sup>4</sup> *Am. Chem. J.*, 28, 121 (1902).

metastatic change into a labile pseudothiohydantoin, and then into a stable isomer.



Three possible formulas, which might be assigned to the labile pseudothiohydantoins, were considered by us, but no conclusive experimental evidence was produced that established any one of these structures:



The structure of the stable phenylpseudothiohydantoin was definitely established by the fact that unsymmetrical benzylphenylthiourea and ethylchloracetate gave the same compound as was obtained by treating the stable phenylpseudothiohydantoin with alkali and benzyl chloride, showing that the phenyl group is attached to the nitrogen outside the ring. This formula was assigned to the phenylpseudothiohydantoin by Dixon.<sup>1</sup>

As we were obliged to discontinue our investigation of this interesting rearrangement on account of lack of time, we stated that we would continue the research at the opening of the next college year. The work was again taken up in this laboratory this year with the intention of examining the behavior of potassium thiocyanate with other chloracetanilides, and incidentally gaining more definite knowledge of the structure of the labile phenylpseudothiohydantoins.

The additional chloracetanilides, which have been studied, have been chloracet- $\beta$ -naphthalide, chloracet-*m*-xylylide, chloracet-*m*-nitranilide, and chloracet-*p*-bromanilide.<sup>2</sup> All of the products

<sup>1</sup> *J. Chem. Soc. (London)*, 71, 620.

<sup>2</sup> "Chloracetparabromanilide suggested itself as a suitable anilide to examine in connection with our work. This was assigned to Mr. H. S. Bristol for investigation, but owing to its poisonous character he was, unfortunately, compelled to stop the investigation. All of the chloracetanilides that we have examined have attacked the skin in a very disagreeable manner, producing symptoms of the same nature as 'poison ivy.' This anilide



obtained have been examined as in the previous paper,<sup>1</sup> in regard to their behavior towards thiolacids and alkali, and also their behavior on heating. The reactions enumerated have served to determine whether we were dealing with a thiocyanate or a labile hydantoin.

What structure is to be assigned to the intermediate products formed in these rearrangements is still left undecided. It is a curious fact that there is no uniformity in the action of potassium thiocyanate on the different chloracetanilides. In one case it is the thiocyanate that has the greater tendency to form, while in another, it is the labile hydantoin. Of the chloracetanilides examined in this paper not one has reacted smoothly with potassium thiocyanate, and given all the three possible products of the reaction. In the metaxylyl derivatives the thiocyanate and stable hydantoin were the only products identified, while from chloracet- $\beta$ -naphthalide the thiocyanate was missing, and only the labile and stable hydantoins were obtained. From chloracet-*m*-nitranilide only one product was identified; this had all the properties of a labile hydantoin.

## EXPERIMENTAL PART.

BY W. K. WALBRIDGE.

*Chloracet- $\beta$ -Naphthalide*,  $\text{ClCH}_2\text{CONHC}_{10}\text{H}_7$ .—This body was obtained by treating chloracetyl chloride with  $\beta$ -naphthylamine. It was moderately soluble in benzene, very soluble in alcohol, but insoluble in water. It is best purified by crystallizing from dilute alcohol, from which it separates in rosettes or fine needles, and melts when pure at  $117^\circ$ - $118^\circ$ . A nitrogen determination gave:

	Calculated for $\text{C}_{12}\text{H}_{10}\text{ONCl}$ .	Found.
Nitrogen.....	6.38	6.42

*Labile  $\beta$ -Naphthylpseudothiohydantoin*.—Chloracet- $\beta$ -naphthalide and potassium thiocyanate reacted immediately when boiled in alcoholic solution. Ten grams of the chloracetnaphthalide and molecular proportions of potassium thiocyanate were boiled in 30 cc. of alcohol for ten minutes; after filtering from potassium chloride, small prisms immediately separated, which melted at  $147^\circ$ , after recrystallization from alcohol. A nitrogen determination proved to be a most violent poison. It seemed to attack the connecting tissue beneath the skin, causing a superficial *eczema*, and thence transmitted to the blood, causing *albuminuria*. The itching did not entirely disappear for over a month."

<sup>1</sup> *Loc. cit.*

tion agreed with the calculated for  $\alpha$ -keto- $\mu$ -imino- $N$ - $\beta$ -naphthyl-tetrahydrothiazole.

	Calculated for $C_{12}H_{10}ON_2S$ .	Found.
Nitrogen.....	11.57	11.62

Several attempts were made to isolate a lower melting isomer by shortening the time of heating, and using varying quantities of alcohol, but no evidence was obtained of any body being formed here except the one isolated melting at  $147^\circ$ , and the stable naphthylpseudothiohydantoin.

*Action of Thioacetic Acid.*—That we were dealing here with a labile hydantoin and not with the first product of the reaction—a thiocyanate—was shown by the action of thioacetic acid. Three grams of the hydantoin and the calculated quantity of thioacetic acid were boiled in 35 cc. of dry benzene for about two hours. Much hydrogen sulphide was evolved during the reaction. The reaction-product, which crystallized out on cooling, was purified by recrystallizing from benzene; it separated in the form of needles and melted when pure at  $139^\circ$ - $140^\circ$ . A nitrogen determination agreed with the calculated for  $\alpha$ -keto- $\mu$ -acetimino- $N$ - $\beta$ -naphthyltetrahydrothiazole.

	Calculated for $C_{16}H_{12}O_2N_2S$ .	Found.
Nitrogen.....	9.86	9.76

*$\beta$ -Naphthylacetthiohydantoinic Acid.*—Accompanying the thiazole derivative described was a small amount of insoluble material, which was purified by repeatedly boiling with fresh benzene. It melted with effervescence at temperatures varying from  $167^\circ$  to  $173^\circ$  according to the rapidity of heating. The behavior on melting, its insolubility in the ordinary solvents, and a nitrogen determination identified this body as naphthylacetthiohydantoinic acid.

	Calculated for $C_{16}H_{14}O_2N_2S$ .	Found.
Nitrogen.....	9.27	9.32

*Behavior on Heating: Stable  $\beta$ -Naphthylpseudothiohydantoin.*—The labile naphthylpseudothiohydantoin showed no strong tendency to pass over into the stable isomer. After heating the dry material for several hours in a boiling water-bath unaltered material was obtained. When the hydantoin melting at  $147^\circ$  was completely melted in an oil-bath, and heated for from ten to fifteen minutes at  $140^\circ$ - $150^\circ$ , a black, vitreous cake was obtained on cool-

ing, from which the impure stable hydantoin was obtained. A smooth rearrangement could not be obtained in this way—the decomposition products interfering with the purification of the stable hydantoin. When the labile hydantoin was boiled for three and one-half hours in dilute alcohol it was converted very smoothly into the stable hydantoin, melting when pure at  $213^{\circ}$ - $214^{\circ}$ , with decomposition. A small amount of the hydantoic acid is also formed at the same time.

*$\beta$ -Naphthylpseudothiohydantoic Acid.*—This acid was prepared by boiling, for one hour, an alcoholic solution of ammonium chloracetate and  $\beta$ -naphthylthiourea. The hydantoic acid separated as an amorphous body and melted with effervescence at temperatures varying from  $195^{\circ}$ - $230^{\circ}$  according to the rapidity of heating. It is insoluble in the ordinary solvents. A nitrogen determination gave:

	Calculated for $C_{18}H_{15}O_2N_2S$ .	Found.
Nitrogen.....	10.77	10.86

*Stable  $\beta$ -Naphthylpseudothiohydantoin.*—This hydantoin was prepared by warming the preceding hydantoic acid on the water-bath with glacial acetic acid for four hours. Water precipitated the hydantoin. It was difficultly soluble in benzene, but crystallized from alcohol in fine needles, and melted when pure at  $213^{\circ}$ - $214^{\circ}$ , with decomposition. A nitrogen determination gave:

	Calculated for $C_{18}H_{15}ON_2S$ .	Found.
Nitrogen.....	11.57	11.65

This stable hydantoin was always deposited during the spontaneous evaporation of the alcoholic filtrates in the preparation of the labile hydantoin. We also observed that the labile hydantoin could be converted very smoothly into the stable hydantoin by boiling for a few minutes with strong hydrochloric acid.

*Action of Alkali on the Stable Hydantoin.*—The stable hydantoin dissolves very easily in warm sodium hydroxide solution. When cooled, the alkaline solution deposits the sodium salt of the stable hydantoin in the form of brilliant spangles. Acetic acid precipitates again the unaltered hydantoin.

*Action of Acetic Anhydride.*—When the stable  $\beta$ -naphthylpseudothiohydantoin was warmed for fifteen minutes in the water-bath with an excess of acetic anhydride a thick paste was obtained; after pouring into water a thick amorphous deposit resulted, which

was very soluble in alcohol, and reprecipitated by water as an oil. The product was finally obtained pure by crystallizing from benzene, from which it separated in fine needles, and melted sharply at  $142^{\circ}$ - $143^{\circ}$ . A nitrogen determination agreed with the calculated for a monoacetyl derivative,  $\alpha$ -keto- $\mu$ - $\beta$ -naphthylimino-*N*-acetetetrahydrothiazole.

	Calculated for Monoacetyl— $C_{10}H_{13}O_2N_2S$ .	Calculated for Diacetyl— $C_{17}H_{14}O_4N_2S$ .	Found.
Nitrogen .....	9.86	8.59	10.27

A quantitative determination of the acetyl groups was made by saponification with standard potassium hydroxide, and titrating the excess of free alkali with standard hydrochloric acid.

Calculated for $(CH_3CO)_1$	Calculated for $(CH_3CO)_2$	Found.
15.14	26.37	12.52

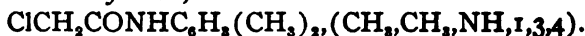
*$\alpha$ -Keto- $\beta$ -benzilidene- $\mu$ -Naphthyliminotetrahydrothiazole.*—

This was obtained by warming in the water-bath, for five hours, the sodium salt of the stable hydantoin with molecular proportions of benzaldehyde in alcoholic solution. It separated from the hot alcohol solution as pale yellow plates, and melted at  $272^{\circ}$  with slight effervescence. A nitrogen determination gave:

	Calculated for $C_{20}H_{14}ON_2S$ .	Found.
Nitrogen .....	8.48	8.43

By D. F. MCFARLAND.

*Chloracet- $m$ -xylidide,*



—This body was obtained by the action of chloracetyl chloride on *m*-xylidine. It crystallized from alcohol in the form of needles and melted at  $151^{\circ}$ - $152^{\circ}$  C. It is very soluble in alcohol, and moderately soluble in benzene. A nitrogen determination gave:

	Calculated for $C_{10}H_{13}ONCl$ .	Found.
Nitrogen .....	7.09	7.26

*Normal Thiocyanacet- $m$ -xylidide,  $NCSCH_2CONHC_6H_3(CH_3)_2$ .*

—When chloracet-*m*-xylidide was boiled with a slight excess of potassium thiocyanate in alcoholic solution for twenty minutes, water precipitated from the alcoholic solution unaltered chloride. After evaporating the aqueous solution *in vacuo* a fair quantity of brilliant prisms separated, which were quite soluble in alcohol, ether, and benzene, and melted at  $98^{\circ}$ . A nitrogen determination agreed with the calculated for *thiocyanacet- $m$ -xylidide*.

	Calculated for $C_{11}H_{12}ON_2S$ .	Found.
Nitrogen .....	12.72	12.97

By further evaporation of the mother-liquor a white granular substance separated, which was insoluble in the ordinary solvents and melted with effervescence at about  $179^{\circ}$ . This was identified as *m*-xylylthiohydantoic acid, identical in properties with that prepared for comparison from *m*-xylylthiourea and ammonium chloracetate. We made attempts to obtain larger yields of the thiocyanate by boiling the chloracet-*m*-xylidide with potassium thiocyanate in alcoholic solution for a longer time, but while less unaltered chloride was obtained by such treatment, the amount of thiohydantoic acid formed was increased, while the yield of thiocyanate was decreased.

*Action of Thioacetic Acid.*—When the thiocyanate melting at  $98^{\circ}$  was boiled with thioacetic acid in benzene solution for a few hours and then allowed to evaporate, a varnish was obtained, which dissolved immediately in cold sodium hydroxide solution. Acetic acid precipitated a mixture of the thiohydantoic acid melting at about  $180^{\circ}$ , and a yellow crystalline body which crystallized from alcohol and melted fairly sharp at  $162^{\circ}$ . Not enough of this was obtained for complete purification and analysis, but its color and solubility in alkali served to identify it as a dithiourethane.

*Behavior on Heating.*—This thiocyanate proved to be very stable when heated in a dry state in the boiling water-bath. After twenty-six hours' heating, it finally completely solidified to a dark red colored body; on crystallizing this from alcohol it separated in clusters of fine needles and melted at  $157^{\circ}$ , the melting-point found for the corresponding stable *m*-xylylpseudothiohydantoin. A similar rearrangement was obtained when the thiocyanate was heated for one hour in an oil-bath at  $145^{\circ}$ . A brown mass was obtained from which was isolated the stable hydantoin.

No indications of the formation of any intermediate labile hydantoin were observed during these experiments. Several attempts were made to isolate a labile hydantoin by boiling the thiocyanate in ether and benzene, but no great change in the melting-point was observed after boiling for seven or eight hours. Slight decomposition usually took place on prolonged boiling. In its

behavior on heating, this thiocyanate is similar to the isomeric thiocyanacetorthoxylidide examined in a previous paper.<sup>1</sup>

*m*-Xylylthiohydantoic Acid.—This acid was made by boiling ammonium chloracetate with *m*-xylylthiourea in alcoholic solution. It separated as a fine white powder, was practically insoluble in the ordinary organic solvents, and melted with effervescence at about 179°-180°. A nitrogen determination gave:

	Calculated for $C_{11}H_{14}O_2N_2S$ .	Found.
Nitrogen .....	11.76	12.40

Stable *m*-Xylylpseudothiohydantoin.—This hydantoin was obtained by heating the above hydantoic acid with glacial acetic acid on the water-bath. It was easily dissolved by hot alcohol, but crystallized on cooling in clusters of needles, which melted at 157°. A nitrogen determination gave:

	Calculated for $C_{11}H_{14}ON_2S$ .	Found.
Nitrogen .....	12.72	12.52

*Action of Alkali.*—When the stable hydantoin was warmed with sodium hydroxide solution it easily dissolved; on cooling, beautiful glistening plates of the sodium salt separated, which gave no definite melting-point.

*Action of Acetic Anhydride.*—When the stable *m*-xylylpseudothiohydantoin was heated with acetic anhydride at 100° for about forty-five minutes a strong red colored solution resulted. Water precipitated a semi-solid which was purified by crystallizing from alcohol. It separated in granular crystals and melted at 165°-166° with slight decomposition. A nitrogen determination agreed with the calculated for a monacetyl derivative of the thiohydantoin.

	Calculated for $C_{12}H_{14}O_2N_2S$ .	Found.
Nitrogen .....	10.68	10.69

In respect to their behavior with acetic anhydride the stable  $\beta$ -naphthyl- and *m*-xylylpseudothiohydantoins are to be classed by themselves in that they both gave monoacetyl derivatives. (Of the stable hydantoins discussed in a previous paper,<sup>1</sup> three—phenyl, orthotolyl, and paratolyl—gave diacetyl derivatives when treated in the same way.

<sup>1</sup> *Loc. cit.*

BY W. B. CRAMER.

*Chloracet-m-nitroanilide*,  $\text{ClCH}_2\text{CONHC}_6\text{H}_4\text{NO}_2$ .—This anilide was prepared from chloracetyl chloride and *m*-nitroaniline. It crystallized from alcohol in plates and melted at  $101^\circ\text{--}102^\circ\text{C}$ . A nitrogen determination gave:

	Calculated for $\text{C}_8\text{H}_7\text{O}_2\text{N}_2\text{Cl}$ .	Found.
Nitrogen.....	13.04	13.03

*Labile m-Nitrophenylpseudothiohydantoin*.—This body was obtained by boiling in benzene chloracet-*m*-nitroanilide with potassium thiocyanate for twenty minutes. It crystallized from alcohol in the form of plates and melted at  $183^\circ\text{--}184^\circ\text{C}$ . A nitrogen determination gave:

	Calculated for $\text{C}_8\text{H}_7\text{N}_3\text{O}_2\text{S}$ .	Found.
Nitrogen.....	17.79	17.60

*Action of Alkali*.—This hydantoin melting at  $183^\circ\text{--}184^\circ$  dissolved in cold sodium hydroxide solution. On neutralizing with acetic acid a mass of needles separated. They were purified by crystallizing from benzene and melted at  $133^\circ\text{--}134^\circ\text{C}$ . A nitrogen determination agreed with the calculated for *m*-nitrophenylcyanamide.

	Calculated for $\text{C}_7\text{H}_6\text{N}_2\text{O}_2$ .	Found.
Nitrogen.....	25.78	25.57

NEW HAVEN, CONNECTICUT,  
February 28, 1903.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

## METHODS FOR THE DETERMINATION OF TOTAL PHOSPHORIC ACID AND POTASH IN SOILS.

BY C. B. WILLIAMS.

Received February 9, 1903.

AGRICULTURAL chemists have seemingly, in recent years, placed too little stress upon the determination of total plant food in soils, as a knowledge of the quantity present is necessary for a thorough understanding of the potentialities, culture methods, and fertilizer requirements of any soil, as well as entering vitally into the interpretations given availability results. With these facts in mind, the writer has, during the past summer, devoted some time to

modifying well-known analytical methods to a reasonably rapid basis for the determination of total phosphoric acid and potash in soils.

#### STUDY OF DIFFERENT SOLVENTS FOR PHOSPHORIC ACID.

The results of work with the action of different solvents on phosphoric acid are incorporated in Table I, and it will be seen

TABLE I.—COMPARISON OF METHODS FOR EFFECTING SOLUTION OF SOIL PHOSPHORIC ACID WHEN 10 GRAMS SOIL ARE EMPLOYED.

Soil. No.	Treated three times with HF and then fused with 10 grams $\text{Na}_2\text{CO}_3$ — $\text{K}_2\text{CO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .	Digested in Kjeldahl flask 1 1/2 hours.							
		Heated on water-bath for 1 1/2 hours.							
		With 30 cc. HCl. Per cent. $\text{P}_2\text{O}_5$ .	With 30 cc. $\text{HNO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .	With 30 cc. $\text{HNO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .	With 30 cc. HCl. Per cent. $\text{P}_2\text{O}_5$ .	With 30 cc. HCl. Per cent. $\text{P}_2\text{O}_5$ .	With 30 cc. HCl followed by digestion 1 hr with 10 cc. $\text{HNO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .	With 40 cc. HCl + 1 gram $\text{KClO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .	With 40 cc. HCl + 1 gram $\text{KClO}_3$ . Per cent. $\text{P}_2\text{O}_5$ .
1	0.0330	0.017	0.016	0.017	0.017	0.017	0.017	0.017	0.017
2	0.0292	0.017	0.014	0.017	0.016	0.015	0.015	0.016	0.017
3	0.0212	0.016	0.014	0.013	0.015	0.015	0.015	0.014	0.012

that the results obtained by the last six modes of treatment are practically identical, and uniformly low, while those by the hydrofluoric acid-fusion method,<sup>1</sup> are perceptibly higher. Fusion of the residues from treatment by the last six methods invariably gave a slight test for phosphoric acid, while, of course, this was not true of the first method, as the residues were entirely decomposed by fusion with sodium and potassium carbonates.<sup>2</sup> The soils were ignited before treatment by the first four methods, but not with the last three.

As the hydrofluoric acid-fusion method gave results uniformly higher, and representing, we think, all the phosphoric acid in the soil, it has been adopted for the determination of total phosphoric acid in soil survey work in North Carolina. It might be objected that higher results by this method are due to the possible presence of ammonium silicomolybdate, as in the dehydration of silica from the fusion with sodium and potassium carbonates there was only one evaporation to dryness; but this would seem unfounded, as

<sup>1</sup> Vide Fresenius, "Quantitative Analysis," pp. 424-426.

<sup>2</sup> *Ibid.*, pp. 422-424.



silica gives no reaction in the cold,<sup>1</sup> and only a strong yellow coloration upon heating.

DETERMINATION OF PHOSPHORIC ACID VOLUMETRICALLY VERSUS GRAVIMETRICALLY.

The volumetric method used is described in this Journal, 23, 8-12,<sup>2</sup> while the gravimetric one employed is the regular official method of the Association of Official Agricultural Chemists. For a test of the relative merits of these two methods of estimating phosphoric acid in soils, where the quantity usually is less than 0.1 per cent., twelve soils (Nos. 23-24) were employed, using solutions obtained by digestion in the water-bath for ten hours with 1.115 sp. gr. hydrochloric acid, shaking thoroughly each hour. The quantity was determined separately in each twelve original and duplicate soils, the total amount from the twelve originals being 0.0260, and from duplicates 0.0280 gram. When the totals of the originals and duplicates were dissolved separately with hydrochloric acid, and redetermined by precipitation with magnesia mixture 0.0199 gram phosphoric acid for originals and 0.0198 for duplicates were obtained.

Results on the same twelve soils by the volumetric method, making determinations separately and adding, gave originals 0.0210 gram phosphoric acid and duplicates 0.0193 gram, which are very close to the composite original and duplicate gravimetric results.

In the light of these results, the volumetric method is considered by far the most accurate for soil work where the percentages of phosphoric acid are usually very low.

SOLUTION OF POTASH IN SOILS.

Results in Table II on soils Nos. 1, 2, and 3 indicate that after ignition and evaporation with hydrofluoric acid five times it is unnecessary to fuse with sodium carbonate, as all potash-bearing silicates have been decomposed, leaving the potash in a form that is easily dissolved by the treatment subsequently given it in the method described elsewhere in this paper.

<sup>1</sup> Fresenius' "Qualitative Analysis," p. 332. F. P. Veitch states, however, that silicic acid gives a yellow coloration in the cold (private communication).

<sup>2</sup> Vide this Journal, 18, 382; *J. Frank. Inst.*, 136, 362; U. S. Dept. of Agriculture, Div. of Chem., Bull. 43, pp. 68-97; *Ibid.*, Bull. 47, pp. 62-82; *Ibid.*, 49, pp. 60-77; *Ibid.*, 51, pp. 47-56; *Ibid.*, Bull. 56, pp. 36-48; *Ibid.*, Bull. 62, pp. 35-41; *Ibid.*, Bull. 56, pp. 36-48; *Ibid.*, Bull. 67, pp. 22-26.

TABLE II.

Soil. No.	Treated five times with HF. Per cent. $K_2O$ .	Treated five times with HF, followed by fusion with $Na_2CO_3$ . Per cent. $K_2O$ .
1	0.204	0.216
2	0.242	0.242
2	0.232	0.232
3	0.187	0.190
3	0.180	0.191

It might be said here that the reason for using the first evaporation with sulphuric acid in the potash method is that a preliminary test upon soils Nos. 6, 11, 13, 15, and 16 worked in duplicate indicated that there was a slight loss in potash if the soils were not saturated with this acid before ignition; the loss probably occurs principally from the volatilization of potash in organic combination.

MOORE'S METHOD.<sup>1</sup>

With reference to the method of Moore for the determination of total potash in soils I found that as long as the combined amount of iron and alumina remained as low as 2 or 3 per cent., it works very well, although in my hands giving slightly low results, but when from 8 to 12 per cent. of iron and alumina are present, trouble comes from caking upon evaporation to a pasty constituency with platinic chloride, the cake not being dissolved by Moore's acid alcohol, even after standing two or three days.

## METHOD FOR THE DETERMINATION OF TOTAL PHOSPHORIC ACID IN SOILS.

Five grams of soil prepared by passing through a sieve with apertures 0.5 mm. in diameter are placed in a platinum dish and ignited until organic matter has been destroyed; then treated three times with hydrofluoric acid, evaporating to dryness each time on a water-bath, using a platinum rod to stir upon each addition of acid. The residue thus obtained is mixed with 10 grams of a mixture of equal parts of sodium and potassium carbonates, and reduced in an agate mortar to a fine powder, after which it is heated over a blast-lamp, gently at first, until the mass has completely agglutinated, when stronger heat is turned on and continued until calm fusion is attained. Then cool and place the dish and its contents in a beaker, and add sufficient (1:1) hydrochloric acid to cover the dish. Place on a water-bath and digest

<sup>1</sup> U. S. Department of Agriculture, Bureau of Chemistry, Circular 9, pp. 5-7.

until the mass has thoroughly loosened from the dish, after which it is removed. Evaporate to dryness on a water-bath and thoroughly dehydrate the silica present by finishing the heating in an air-bath at  $110^{\circ}$  C. for four or five hours. Take up with dilute hydrochloric acid and digest on water-bath for twenty to thirty minutes, after which filter from silica, washing the same thoroughly to remove last traces of phosphoric acid. To the filtrate is added sufficient nitric acid to liberate all hydrochloric acid, and the solution is evaporated to a volume of about 40 cc. Then neutralize the excess of nitric acid with ammonia, and add 10 to 12 grams of ammonium nitrate. After cooling, 30 cc. of recently filtered molybdic solution are added and the phosphoric acid precipitated by shaking in a Wagner machine, and determined volumetrically.<sup>1</sup>

#### METHOD FOR THE DETERMINATION OF TOTAL POTASH IN SOILS.

After saturating 4 grams of soil in a platinum dish thoroughly with dilute (1:1) sulphuric acid, dispel the excess of acid by gentle heat over a low flame, exercising care that no loss occurs from spurting. Next treat with 2 to 3 cc. hydrofluoric acid (free from potash) five times, using a platinum rod to stir occasionally, and evaporate each time to apparent dryness on a water-bath, but just before going to dryness the last time 1 cc. dilute sulphuric acid is added and the heating continued until practically all hydrofluoric acid and water have been driven off. The dish is then heated over a small flame until the evolution of sulphur trioxide ceases. When this is finished, about 20 cc. distilled water, slightly acidified with hydrochloric acid, is added, and digested on a water-bath, stirring occasionally until the liquid has been reduced to about one-third of its original volume. By this time complete solution of the potash has been effected, and the whole contents of the dish are transferred with water to a 200 cc. graduated flask, which is afterwards heated on a water-bath to near boiling, when ammonia and ammonium oxalate are added in sufficient quantities to precipitate all iron, alumina and calcium present (2 cc. have been found sufficient). Allow the solution to cool, shaking two or three times during cooling to reduce the error of occlusion as much as possible. The volume is then made to 200 cc., and an aliquot portion correspond-

<sup>1</sup> This Journal, 23, 8-12.

ing to 2 grams of soil is filtered off into a porcelain dish and evaporated to semi-dryness on a water-bath, finishing by heating cautiously over a gentle flame, being careful that loss occurs neither from creeping nor decrepitation. When dry, ignite gently to decompose oxalates and expel ammonium salts. Take up with 10 to 15 cc. of hot distilled water, acidify with 3 or 4 drops of hydrochloric acid, and filter. Determine the potash in the filtrate by precipitation with chloroplatinic acid, etc., as directed in the regular Lindo-Gladding method.

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[CONTRIBUTION FROM THE UNIVERSITY OF ILLINOIS, AGRICULTURAL  
EXPERIMENT STATION, No. 9.]

**IMPROVED METHOD FOR SEPARATION AND DETERMINATION OF TOTAL ALKALIES IN SOILS.**

By J. H. PETTIT.

Received February 13, 1903.

WHILE working upon soils in this laboratory, considerable difficulty was found in the determination of the total alkalies. The method used was that outlined in the "Methods of Analysis of the Association of Official Agricultural Chemists." By this method the iron, aluminum, phosphorus, and magnesium are removed from the hydrochloric acid solution by precipitating with barium hydroxide. From the filtrate, barium and calcium are precipitated by ammonium hydroxide and ammonium carbonate. This filtrate is evaporated to dryness, the ammonium salts driven off, and the residue taken up with a little hot water. Ammonium carbonate is again added to remove the last traces of barium, the solution filtered, the filtrate evaporated to dryness in platinum dishes, and the chlorides of the alkalies ignited.

It was found, however, that considerable barium carbonate remained with the ignited alkalies. This appeared as a thin white layer in the bottom of the platinum dishes, when hot water was added. Also, by the addition of ammonium carbonate to this more concentrated solution, more barium was precipitated. This process of precipitation, filtration, and evaporation was necessarily repeated five or six times before a constant weight of chlorides was obtained. Further, it was found that in this solution, in which ammonium carbonate finally gave no precipitate, the addition of a solution of ammonium sulphate gave a precipitate of

barium sulphate. Ten determinations of the barium in such solutions gave the following weights of barium sulphate:

	Gram.		Gram.
1.....	0.0065	6.....	0.0080
2.....	0.0083	7.....	0.0113
3.....	0.0088	8.....	0.0107
4.....	0.0075	9.....	0.0099
5.....	0.0061	10.....	0.0111

As the weight of the total alkalies is often under 20 mg. the presence of such amounts of barium would give rise to considerable error in the determination. Accordingly, the usual method was modified as follows: Just previous to evaporating the solution of the chlorides, in platinum dishes, a few cubic centimeters of an ammonium sulphate solution—75 grams to the liter—are added. The precipitate is filtered out and the filtrate evaporated as usual, in platinum dishes, and ignited. In this way, the barium is completely removed at one operation, and the alkalies are changed into sulphates, which can be ignited over the full heat of the Bunsen burner without danger of loss through volatilization. The evaporation, however, must be to complete dryness, otherwise there is danger of loss, through the decrepitation of the sulphates upon ignition. After igniting to a red heat, about 1 gram of dry, powdered ammonium carbonate is added to the dish and volatilized, thus breaking up any acid sulphates which may have formed.

As a check upon the possibility of loss through volatilization, during the ignition, four determinations of the sodium, the more volatile of the two alkalies, as sulphate in a solution of chemically pure sodium chloride, gave the following weights of sodium sulphate: 0.0291, 0.0292, 0.0291 and 0.0290 gram. Repeated ignition over the Bunsen burner did not alter these weights. The weight of sodium sulphate, calculated from the weight of sodium chloride used, was 0.02916 gram.

Below are some duplicate determinations of total alkalies obtained by this method, in our ordinary work:

Total alkalies.			Total alkalies.		
	Gram.	Gram.		Gram.	Gram.
1.....	0.0191	0.0187	9.....	0.0632	0.0636
2.....	0.0383	0.0378	10.....	0.0331	0.0331
3.....	0.0288	0.0283	11.....	0.0325	0.0328
4.....	0.0285	0.0286	12.....	0.0410	0.0411
5.....	0.0332	0.0326	13.....	0.0224	0.0221
6.....	0.0128	0.0130	14.....	0.0215	0.0219
7.....	0.0324	0.0320	15.....	0.0197	0.0196
8.....	0.0124	0.0123	16.....	0.0277	0.0283

The advantages of this modified method are that the alkalies are entirely freed from barium in one operation and are transformed into sulphates, which do not present the difficulties of ignition found with the chlorides.

UNIVERSITY OF ILLINOIS AGRICULTURAL  
EXPERIMENT STATION.

### DOES CHOLESTEROL OCCUR IN OLIVE OIL?

BY AUGUSTUS H. GILL AND CHARLES G. TUFTS.

Received February 20, 1903.

UPON this question there has been much uncertainty. Beneke<sup>1</sup> stated in 1862 that he believed he had obtained cholesterol from olive oil though the amount was too small to admit of proof. Salkowski<sup>2</sup> in 1887 found the amount obtainable from 50 grams too small for a determination of the melting-point, though the color reactions of phytosterol were given, and he expressed the opinion that olive oil contained neither phytosterol nor cholesterol but that the small amount present in the sample examined by him was due to the presence of olive kernel oil. Gerard<sup>3</sup> reported in 1892 that he had obtained phytosterol from olive oil and had identified it by the melting-point. Bömer<sup>4</sup> declared in 1898 that from two samples of Provence oil he had obtained an alcohol whose melting-point and crystal form left its identity with phytosterol beyond question. In the same year, however, Lewkowitsch<sup>5</sup> stated definitely that "The unsaponifiable matter occurring in olive oil is cholesterol, whereas all other vegetable oils contain phytosterol," and in 1898, Allen<sup>6</sup> also stated that "it (cholesterol) occurs in olive oil" and again that "Phytosterol is found in most vegetable oils with the notable exception of olive and palm." That Allen was not unfamiliar with the work of Bömer seems evident from the fact that he refers to the article in which the latter's work is described. Soltsien in 1901 reported the detection of phytosterol in olives from Bari pressed by himself.<sup>7</sup>

In view of the fact that the matter was of interest not only from

<sup>1</sup> *Ann. Chem. Pharm.*, 122, 249-255.

<sup>2</sup> *Ztschr. anal. Chem.*, 26, 581.

<sup>3</sup> *Compt. rend.*, 114, 1544-1546.

<sup>4</sup> *Ztschr. Unter. Nahr. u. Genuss.* (1898), pp. 81-96.

<sup>5</sup> "Chemical Analysis of Oils, Fats and Waxes," second edition, p. 452.

<sup>6</sup> "Commercial Organic Analysis," third edition, Vol. II, Part 1, pp. 347 and 351.

<sup>7</sup> *Chem. Centrbl.*, 72, II, 243 (1901).

a purely scientific standpoint but also might be of importance in the detection and analysis of an important oil, it seemed desirable that the question should receive further consideration.

The oil first examined was the ordinary green oil of commerce used as a wool oil. Three portions, each of 1.5 kilos, were treated according to the method described in our article upon maize oil.<sup>1</sup> The unsaponifiable matter so obtained was small in amount and appeared to consist largely of coloring-matter and other substances quite dissimilar from either phytosterol or cholesterol. After several saponifications with alcoholic potash and repeated washing with water, the residue was a highly colored semiliquid grease from which no crystals could be obtained either by precipitation, successive treatment with small portions of alcohol, or slow evaporation from solution in either strong or dilute alcohol. The color reactions of this group of compounds were given in all cases. The residues from the three portions of oil were combined and boiled an hour with an excess of benzoyl chloride; the product was washed with small portions of alcohol and saponified. After two recrystallizations, the partially purified alcohol was boiled with an excess of acetic anhydride; on washing the resulting acetate with alcohol and then saponifying, a crystalline substance was obtained which, though small in amount and still too impure for a determination of the melting-point, consisted of the easily recognizable six-sided plates characteristic both of phytosterol and of sitosterol.

As the evidence afforded by the above examination was inconclusive, it seemed important to obtain an olive oil which should contain the substance sought in greater quantity; it was thought that this would be the case with oils drawn from the most mature fruits. An oil was therefore chosen which had been pressed from fully ripened olives; it was a Californian virgin oil of a light yellow color and strong heavy taste. The specific gravity at 15° C. was 0.917 and the iodine value 83.5; the oil was of known origin and quite free from any adulteration.

One kilo of this oil, extracted as before, yielded at once a light yellow crystalline mass which, after a second saponification and washing, was recrystallized from alcohol. The yield of impure crystals was 0.093 per cent.

To determine whether the finally purified alcohol was a single

<sup>1</sup> This Journal, 25, 254.

compound or had been mixed with other substances, the mother-liquors from the various recrystallizations were themselves recrystallized. All yielded crystals identical in form; the melting-points were a trifle lower than that of the main portion, but this may be due to the fact that as the amounts were smaller they could not be quite as completely purified. The variation was in no case greater than  $2^{\circ}$ . The crystals obtained from the mother-liquors were used in preparation of the esters as well as the main portion.

The bromide was made by treatment of the solution in carbon tetrachloride with a dilute solution of bromine: the action was slow. Half an hour after the bromine had been added, apparently in slight excess, the solution was completely decolorized and two further additions of bromine were followed by the same result. The melting-point was not determined, as purification was difficult and the compound turned black on standing.

The acetate was prepared by boiling an hour with an excess of acetic anhydride, and formed oblong flat plates melting at  $120.3^{\circ}$ - $120.7^{\circ}$ .

The propionate was prepared similarly from propionic anhydride and also formed oblong plate crystals; the melting-point was  $102.5^{\circ}$ - $103.5^{\circ}$ .

The benzoate, like the preceding esters, was made from the anhydride and formed oblong plates; it was noticed that in some cases the longer sides were apparently not quite parallel. The melting-point was  $145^{\circ}$ - $145.5^{\circ}$ .

The melting-point of the alcohol itself, even when pure, was found to vary somewhat with the conditions under which it was taken. When first prepared and dried at  $100^{\circ}$ , the melting-point was  $134^{\circ}$ - $134.5^{\circ}$ ; some days later, after exposure to the air, it was found to be  $132^{\circ}$ - $133^{\circ}$ . To examine this depression more closely, the propionate, which had been carefully purified, was saponified; the product rapidly recrystallized five times by chilling the solution in hot alcohol, and the crystals were then dried at  $100^{\circ}$ . The melting-point, determined immediately, was  $135^{\circ}$ - $135.5^{\circ}$ ; after twenty-four hours it was found to be  $133^{\circ}$ - $133.5^{\circ}$  and after seventy-two hours  $132.5^{\circ}$ - $133^{\circ}$ . In this connection it may be of interest to state that although no such rapid fall was noticed in the case of the sitosterol from maize oil, a portion of this latter substance, which originally melted at  $138^{\circ}$ , examined



about eighteen months after preparation, having been protected meanwhile from light, showed a melting-point of  $128^{\circ}$ - $130^{\circ}$ .

A sample of phytosterol from olive oil which had been prepared by twice saponifying the propionate melting at  $101.5^{\circ}$ - $103.5^{\circ}$  and recrystallizing the product three times, showed, two weeks after preparation and after five days' heating in a dark closet at about  $90^{\circ}$  C., a melting-point of  $99^{\circ}$ - $103^{\circ}$ ; the melting-point of the same sample after about six hours' heating was  $127^{\circ}$ - $129^{\circ}$ . The phytosterol showed as a result of the longer heating a faint yellow color. The melting-point, in all cases, was determined in a straight capillary tube attached to the stem of a small bulbed thermometer suspended in a 150 cc. flask of concentrated sulphuric acid. The flask was supported about an inch above an iron plate which was heated by a small flame. The temperature was brought fairly rapidly to within  $15^{\circ}$  to  $20^{\circ}$  of the melting-point and the rise was then reduced to about  $2^{\circ}$  a minute. When within  $2^{\circ}$  or  $3^{\circ}$  of the melting-point, the rate was made about  $0.2^{\circ}$  a minute and was there maintained until melting was complete. This observed depression of the melting-points may perhaps explain the varying values recorded in the literature. The crystal form of the alcohol from olive oil closely resembled that of the sitosterol from maize oil. The color reactions of the two compounds were the same. The identification of the compound is the more difficult because observers have disagreed upon the melting-points of these alcohols as well as upon their esters.

The following table shows the melting-points which would seem to be the most trustworthy given by various investigators for phytosterol, sitosterol, cholesterol and the body from olive oil, and their esters.

	Cholesterol.	Phytosterol.	Sitosterol.	Alcohol from olive oil.
Alcohol .....	146°-147° <sup>1</sup>	132°-136° <sup>4</sup> 136-141.5° <sup>5</sup>	137.5° <sup>2</sup> 136.5° <sup>3</sup> 138°	135°-135.5° <sup>6</sup> 135-136.5° <sup>7</sup> 135.5-136.5° <sup>8</sup>
Acetate.....9...	113-114° <sup>2</sup>	120° <sup>4</sup> 117-126° <sup>7</sup> 123.5-135° <sup>8</sup> 120-121° <sup>9</sup>	127° <sup>4</sup> 127.1° <sup>9</sup>	120.3-120.7° <sup>9</sup>
Benzoate .....	145-145.5° <sup>3</sup>	142-146° <sup>3</sup> 144-147° <sup>7</sup>	145-145.5° <sup>11</sup> 142-142.5° <sup>9</sup>	145-145.5° <sup>9</sup>
Propionate .....	97-98° <sup>3</sup>	104-116° <sup>3</sup>	108.5° <sup>3</sup> 108.4° <sup>9</sup>	102.5-103.5° <sup>9</sup>

The melting-points in the above table would seem conclusive evidence that the alcohol from olive oil is not cholesterol. Though the benzoates of the two compounds have the same melting-point, the olive oil compound did not show the double melting-point characteristic of cholesterol benzoate and gave oblong plate crystals, while cholesterol benzoate crystallizes in quadratic tables.<sup>1</sup> Furthermore, the propionate was carefully examined for the play of colors on cooling, stated by Obermüller<sup>12</sup> to be an easily recognizable and characteristic test for cholesterol, and no colors were detected. The difference in the manner of growth and in the crystalline form of the olive oil alcohol and of the cholesterol from wool grease, which was examined simultaneously, is quite unmistakable.

The further identification is rendered difficult by the fact that under the general term "phytosterol" have been included alcohols which it seems probable are not identical. Thus the alcohols from rapeseed oil and from cottonseed oil are both called "phytosterol," though the melting-points of the acetates are in one case 134°-135° and in the other 123.5°-124°.

In the following table are brought together the values for sito-

<sup>1</sup> Reinitzer: *Monatsh. Chem.*, 9, 421 (1888).

<sup>2</sup> Mauthner and Sulda: *Ibid.*, 18, 367 (1894).

<sup>3</sup> Ritter: *Ztschr. physiol. Chem.*, 34, 461.

<sup>4</sup> V. Lipman: *Ber. d. chem. Ges.*, 20, 3201 (1887).

<sup>5</sup> Hesse: *Ann. Chem. (Liebig)*, 192, 175.

<sup>6</sup> Hesse: *Ibid.*, 228, 296 (1885).

<sup>7</sup> Jacobson: *Ztschr. physiol. Chem.*, 13, 32 (1889).

<sup>8</sup> Bömer and Winter: *Ztschr. Unter. Nahr. u. Genuss.*, 4, 864 (1901).

<sup>9</sup> Gill and Tufts: *This Journal*, 28, 254.

<sup>10</sup> Gerard: *Compt. Rend.*, 114, 1544 (1892).

<sup>11</sup> Bömer: *Ztschr. Unter. Nahr. u. Genuss.*, (1898), p. 81.

<sup>12</sup> *Ztschr. physiol. Chem.*, 18, 39 (1891).

sterol from maize oil and from wheat, for the alcohol from olive oil, and for the phytosterol from cottonseed oil.

	Sitosterol.	Alcohol from olive oil.	Phytosterol.
Alcohol .....	136.5 <sup>0</sup> -138 <sup>0 1/2 1/3</sup>	135 <sup>0</sup> -136.5 <sup>0 1/2 1/3</sup>	136 <sup>0</sup> -137 <sup>0 5</sup>
Acetate .....	127 <sup>1 1/3</sup>	120.3-120.7 <sup>3</sup>	123.5-124 <sup>5</sup> 120-121 <sup>3</sup>
Propionate .....	108.5 <sup>1 1/3</sup>	102.5-103.5 <sup>3</sup>	104-105 <sup>5</sup>
Benzoate .....	142-145.5 <sup>1 1/2 1/3</sup>	145-145.5 <sup>3</sup>	142-143 <sup>5</sup>

While the differences here are less marked than in the case of the olive oil alcohol and cholesterol, the melting-points seem, on the whole, to indicate that the compound from olive oil resembles the phytosterol from cottonseed oil more than sitosterol from maize oil or from cereals, and is undoubtedly phytosterol and not cholesterol.

## THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.

BY L. M. DENNIS AND J. G. O'NEILL.

Received February 8, 1903.

IN 1891 Hempel and Dennis described a method<sup>1</sup> for the volumetric determination of certain hydrocarbons that are usually present in illuminating gas. Up to that time, all hydrocarbons in this product, with the exception of methane, had been determined by absorption with fuming sulphuric acid and had been classed under the general term "heavy hydrocarbons." It is true that Bunsen<sup>7</sup> gives an analysis of illuminating gas in which the percentages of benzene, ethylene and propylene are stated, but the amounts of these three gases were calculated by means of equations from the results of explosions with air and oxygen, and the calculation was based upon the assumption that the heavy hydrocarbons in the gas consisted only of ethylene, propylene and benzene. It was ascertained by Hempel and Dennis that certain hydrocarbons such as benzene and naphthalene could be removed, in part at least, by means of absolute alcohol, the remainder of the heavy hydrocarbons being then absorbed by fuming sulphuric acid and the methane being finally determined by explosion or combus-

<sup>1</sup> Mauthner and Suida: *Monatsh. Chem.*, 18, 367 (1894).

<sup>2</sup> Ritter: *Ztschr. physiol. Chem.*, 24, 461.

<sup>3</sup> Gill and Tufts: *This Journal*, 28, 254.

<sup>4</sup> Bömer: *Ztschr. Unter. Nahr. u. Genuss.* (1898), p. 81.

<sup>5</sup> Bömer and Winter: *Ibid.*, 4, 864 (1901).

<sup>6</sup> *Ber. d. chem. Ges.*, 24, 1162.

<sup>7</sup> "Gasometrische Methoden," second edition, (1877), p. 142.

tion. In 1894 Noyes and Blinks adapted<sup>1</sup> the method of Hempel and Dennis to the Bunte burette.

Recent work in this laboratory, however, has shown that while the absorption of benzene by means of alcohol may sometimes give agreeing results, the removal of the benzene is usually by no means complete and the results, at times, show wide variations. The following analyses are given in confirmation of this statement. Air was drawn into a Hempel burette containing water as the confining liquid, and was measured. It was then passed into a gas pipette containing benzene and was drawn back into the burette and the increase in volume noted. The mixture of benzene and air was next passed into a pipette containing mercury and 3 cc. of absolute alcohol, and was shaken for three minutes in contact with the alcohol. The residue was then drawn back into the burette and was passed into a pipette filled with water and was shaken with that liquid for three minutes to remove the vapor of alcohol. The gas was now drawn back into the burette and measured. The results were:

TABLE I.

	I. cc.	II. cc.	III. cc.
Air taken .....	67.0	50.0	52.2
Air plus benzene ( $C_6H_6$ ) .....	73.0	54.0	57.0
After shaking with alcohol .....	69.0	51.8	54.2
After shaking with water .....	68.4	51.4	53.7
Benzene taken .....	6.0	4.0	4.8
Benzene found .....	4.6	2.6	3.3

Experiments were next tried to ascertain whether repeated treatment with alcohol would remove all of the benzene, and, as will be seen from the table below, it appears that this reagent is unable to remove benzene completely from mixtures of that substance with air.

TABLE II

	I. cc.	II. cc.	III. cc.	Fresh absolute alcohol.	
				IV. cc.	V. cc.
Air taken .....	58.6	60.1	63.0	56.8	67.9
Air plus benzene .....	62.8	64.6	67.0	61.0	72.8
After shaking with alcohol .....	59.8	61.6	63.8	57.8	69.0
After shaking with water .....	59.4	61.1	63.8	57.6	68.8
After second shaking with alcohol .....	59.2	↓	↓	....	....
After second shaking with water .....	59.1			....	....
After third shaking with alcohol .....	59.1			....	....
After third shaking with water .....	59.1			....	....
After passing residue into fuming sulphuric acid and then into the potassium hydroxide pipette .....	58.7	60.2	62.9	....	....

<sup>1</sup> This Journal, 16, 697.

It was therefore apparent from these results that for the complete and speedy removal of benzene from illuminating gas some absorbent other than absolute alcohol must be employed.

In 1897 Hofmann and Küspert described<sup>1</sup> certain compounds of hydrocarbons with metallic salts and stated that when illuminating gas acts upon a mixture of nickel hydroxide and aqua ammonia, there results a compound of nickel cyanide with ammonia and benzene,  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$ . This statement led the authors of the present paper to examine into the action of an ammoniacal nickel solution upon benzene with the view to ascertaining whether a method could be developed for the volumetric determination of the benzene that is present in the form of vapor in gas mixtures. Sufficient of the absorbent to fill a Hempel simple absorption pipette (about 150 cc.) was prepared by dissolving 25 grams of crystalline nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in 50 cc. of water and adding 50 cc. of strong aqua ammonia. The solution was allowed to cool, was decanted from any salt that separated out and strong aqua ammonia was then added until the volume amounted to 150 cc. The solution loses its efficiency if diluted with water, and its absorptive power is greatly diminished if nickel hydroxide is present in suspension. The analytical results given in this paper were obtained with the reagent prepared in this manner. Experiments showed that this solution absorbed nothing from air, but that when shaken with a volume of air it gave off a small amount of ammonia gas. In the first series of experiments it was sought to remove this ammonia by passing the gas mixture into a Hempel pipette filled with water, but, since this did not entirely remove the ammonia, it was found necessary to use in place of the water a 5 per cent. solution of sulphuric acid.

Later experiments made in this laboratory by Mr. W. C. Geer have shown that it is possible to prepare the reagent in such manner as to do away with the necessity of the treatment of the gas mixture with dilute sulphuric acid. The method of preparation of the reagent is as follows: Forty grams of nickel nitrate are dissolved in 160 cc. of water to which has been added 2 cc. of nitric acid of specific gravity 1.44. This solution is poured slowly with constant stirring into 100 cc. of ammonium hydroxide, specific gravity 0.908. The resulting deep blue solution is used in the absorption. It has a very slight tinge of lavender. The odor of

<sup>1</sup> *Ztschr. anorg. Chem.*, 18, 204.

ammonia is noticeable, but is not strong. The few analyses that have been made with the reagent prepared in this manner indicate that it is similar in action to that prepared as above described and that it is equally efficient. It should, however, be more thoroughly tested before complete reliance is placed upon it.

In the series of experiments described in the following pages, the analyses were carried out in a "simple" Hempel burette provided with a water jacket, and water was used as the confining liquid.

Experiments were first made to ascertain whether benzene vapor mixed with air can be quantitatively absorbed by the ammoniacal nickel solution just described. The gas mixture was first passed into a pipette containing the ammoniacal nickel solution and was shaken with that reagent for three minutes. It was then drawn back into the burette, passed into a pipette containing mercury and 5 cc. of 5 per cent. sulphuric acid and was shaken for three minutes, being then drawn back and measured.

TABLE III.

	I. cc.	II. cc.	III. cc.
Air taken .....	52.7	48.6	51.3
Air plus benzene.....	56.4	52.4	55.2
After shaking with ammoniacal nickel nitrate solution.....	53.2	49.0	51.9
After shaking with 5 per cent. sulphuric acid.....	52.7	48.6	51.3
Benzene taken.....	3.7	3.8	3.9
Benzene found.....	3.7	3.8	3.9

The above results show that benzene vapor is quantitatively absorbed by treatment with an ammoniacal nickel solution prepared as above, when the gas mixture is shaken with the reagent for three minutes. Results of approximate accuracy can be obtained by using a simple burette without water jacket, but there seems to be a slight heating of the gas mixture resulting from the absorption of the ammonia gas by the dilute sulphuric acid, this rise in temperature being sufficient to cause appreciable error in the final reading. To ascertain whether the time necessary for the absorption of the benzene could be reduced, other mixtures of benzene and air were prepared and were shaken with the absorbent for one minute, for two minutes, and for three minutes. The results, which need not here be inserted, showed that a three-minute shaking of the gas mixture with the absorbent is necessary for the complete removal of the benzene.

The next point to be ascertained was whether the nickel solution would absorb other constituents of illuminating gas and would so interfere with their determination as to render its use for the absorption of benzene impossible. Measured amounts of carbon dioxide were mixed with measured amounts of air and this mixture was passed into a pipette containing the nickel solution. As was to be expected, the carbon dioxide was completely removed. It had already been found that the nickel solution had no effect upon air, and consequently the absorption of oxygen in the illuminating gas by this reagent did not need further examination. To ascertain whether carbon monoxide and the unabsorbable residue, consisting chiefly of methane, hydrogen and nitrogen, is affected by the nickel solution, the heavy hydrocarbons were removed from 100 cc. of illuminating gas by means of fuming sulphuric acid and potassium hydroxide, and the residue was then shaken for three minutes with the nickel solution and then with the dilute sulphuric acid. No diminution in volume resulted. From these experiments it appears that the ammoniacal nickel solution beyond removing, wholly or in part, the hydrocarbons other than methane, absorbs no other gas except carbon dioxide, but the fact that this last-named gas is removed by the reagent makes it impossible to use the nickel solution for the removal of benzene and allied carbons, and still adhere to the order that is usually followed.<sup>1</sup> In the customary procedure the hydrocarbon vapors are first absorbed by alcohol, then carbon dioxide by caustic potash, and then the so-called heavy hydrocarbons by fuming sulphuric acid. Hempel and Dennis state<sup>2</sup> that carbon dioxide may not first be removed by means of potassium hydroxide because benzene is soluble in that reagent. Experiments were made to ascertain whether this statement is correct. A measured volume of air was mixed with a measured volume of benzene vapor and this mixture was passed over into a pipette containing potassium hydroxide. No diminution in volume resulted. It therefore appears that the absorption of carbon dioxide by potassium hydroxide may properly precede the absorption of benzene. To be perfectly sure upon this point, however, the following experiment was made: Three Muencke wash-bottles containing clear barium hydroxide solution were connected together and illuminating gas was passed through

<sup>1</sup> Hempel-Dennis's "Gas Analysis" (1902), p. 282.

<sup>2</sup> *Ibid.*, p. 281.

this chain. The carbon dioxide present in the gas was completely removed by the reagent in the first bottle. The gas issuing from the third bottle was therefore free from carbon dioxide, but could safely be assumed to contain some of all of the other constituents of illuminating gas. 100 cc. of the gas issuing from the third bottle was drawn off into a Hempel burette and was then passed over into the caustic potash pipette. No decrease in volume took place. A repetition of this experiment gave the same result, and there was thus obtained confirmation of the statement made above, that potassium hydroxide removes nothing from illuminating gas except carbon dioxide.

Experiments were next undertaken to ascertain, if possible, the nature of the hydrocarbons removable by alcohol and by the ammoniacal nickel solution. These hydrocarbons probably consist largely of ethylene, propylene, and benzene. Ethylene was prepared by treating pure ethylene bromide with a zinc-copper couple. The purity of the gas was tested by passing it into fuming sulphuric acid, the confining water in the burette having first been saturated with the ethylene. Ten cc. of the gas left a residue of 0.2 cc., showing a purity of 98 per cent. Measured volumes of air were now mixed with measured volumes of this gas and the mixture was then passed into a pipette containing the nickel solution and then into a pipette containing mercury and 5 cc. of 5 per cent. sulphuric acid. The results obtained were:

TABLE IV.

	I. cc.	II. cc.	III. cc.
Air taken.....	49.2	51.5	48.0
Air plus ethylene .....	58.0	60.8	54.2
After shaking with ammoniacal nickel nitrate solution.....	58.8	62.4	55.1
After shaking with 5 per cent. sulphuric acid.....	57.9	60.9	54.2

It therefore appearing that ethylene is not taken up by the nickel solution, experiments were next carried out to ascertain whether benzene and ethylene could be separated by means of the nickel solution. The results of these experiments follow:

TABLE V.

	I. cc.	II. cc.	III. cc.	IV. cc.
Air taken.....	50.2	60.7	48.9	54.4
Air plus benzene.....	53.0	64.2	51.1	57.2
Air plus benzene plus ethylene.....	57.6	68.7	57.2	64.4
After shaking with ammoniacal nickel nitrate solution and then with 5 per cent. sulphuric acid .....	54.7	65.2	54.9	61.6



	I. cc.	II. cc.	III. cc.	IV. cc.
Benzene taken.....	2.8	3.5	2.2	2.8
Benzene found.....	2.9	3.5	2.3	2.8
After shaking the residue with absolute alcohol and then with water.....	53.4	64.6	54.7	61.1
After treatment with fuming sulphuric acid and then with potassium hydroxide .....	50.7	61.3	49.7	55.3
Ethylene taken (88 per cent. pure).....	4.6	4.5	6.1	7.2
Ethylene found by alcohol.....	1.3	0.6	0.2	0.5
Ethylene found by fuming sulphuric acid and potassium hydroxide after alcohol.....	2.7	3.3	5.0	5.8
Total ethylene found .....	4.0	3.9	5.2	6.3
Ethylene taken (corrected volume) .....	4.04	3.9	5.36	6.3

The results in Table V show that a satisfactory separation of benzene from ethylene and probably from the other hydrocarbons of the ethylene series may be effected by first shaking the gas mixture with the ammoniacal nickel nitrate solution for three minutes, and then with a 5 per cent. solution of sulphuric acid for the same length of time.

It was hoped that it might be possible to remove the ethylene series of hydrocarbons by means of absolute alcohol before subjecting the illuminating gas to treatment with fuming sulphuric acid. If this were possible, the hydrocarbons would be divided, analytically, into three distinct groups; and a much clearer idea of the illuminants in the gas could then be obtained from the results of a volumetric analysis than is possible under the present methods. The results in Table V have shown that the absorption of ethylene by alcohol is far from complete, and, moreover, that the results of such absorption are by no means constant. It was thought desirable, however, before abandoning the separation by alcohol to try the method with illuminating gas, and in Table VI the results of these experiments are given.

TABLE VI.

	I. cc.	II. cc.	III. cc.	IV. cc.
Carbon dioxide.....	1.2	1.2	1.1	1.1
Benzene by nickel solution and dilute sulphuric acid .....	1.2	1.0	1.0	1.0
Hydrocarbons removed by absolute alcohol and water .....	1.5	0.3	1.3	0.5
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide.....	2.3	3.5	2.6	3.4
Total hydrocarbons absorbed by the three reagents.....	5.0	4.8	4.9	4.9

These results demonstrate conclusively that absorption by alcohol can not be employed for the purpose in hand and that at the present time the gas analyst must content himself with the absorption of benzene by the nickel solution and the subsequent absorption of the so-called heavy hydrocarbons by fuming sulphuric acid. In Table VII are given four analyses of illuminating gas, showing the accuracy of the determinations of carbon dioxide, benzene, and the heavy hydrocarbons.

TABLE VII.

	I. cc.	II. cc.	III. cc.	IV. cc.
Carbon dioxide .....	1.2	1.2	1.2	1.2
Benzene by nickel solution and dilute sulphuric acid .....	1.0	1.0	0.9	0.9
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide.....	4.0	3.9	3.9	4.0
Total hydrocarbons.....	5.0	4.9	4.8	4.9

Before the ammoniacal solution of nickel nitrate and the 5 per cent. solution of sulphuric acid are used for the absorption of benzene, the reagents should, of course, be saturated with the other constituents of the gas mixture in the usual manner.<sup>1</sup> If the reagents in the pipettes have been used for analysis of illuminating gas, they should not be used in the examination of generator gas or of any other gas mixture differing appreciably from the illuminating gas, for the gases that have been dissolved by the reagent when it was shaken with the illuminating gas would escape into another superimposed gas mixture, if this latter did not contain these dissolved gases at approximately the same partial pressure as that at which they existed in the gas with which the reagent was first shaken. Consequently the gas pipettes should be filled with fresh solutions of ammoniacal nickel nitrate and sulphuric acid whenever the gas mixture to be analyzed differs markedly from that for which the reagents had previously been used.

The results may briefly be summarized as follows:

(1) Under the described conditions, alcohol does not completely remove either benzene or ethylene from gas mixtures.

(2) The use of an ammoniacal solution of nickel nitrate furnishes a rapid and exact method for the determination of benzene

<sup>1</sup> Hempel-Dennia's "Methods of Gas Analysis," (1902), p. 119.

in mixtures of that substance with air and ethylene, and in coal gas.

The authors would recommend that in the analysis of illuminating gas (coal gas), the order of procedure be: (a) The absorption of carbon dioxide by potassium hydroxide; (b) the absorption of benzene by the ammoniacal solution of nickel nitrate above described; (c) the absorption of the "heavy hydrocarbons" by fuming sulphuric acid; (d) the absorption of oxygen by alkaline pyrogallol or by phosphorus; (e) the absorption of carbon monoxide by cuprous chloride; and (f) the determination of the methane and hydrogen.

The authors have been unable to try this new method on any commercial gas mixture other than the local supply of illuminating gas. They would therefore earnestly request chemists using the method on other gas mixtures to communicate to them the results of such analyses and call their attention to any difficulties that may arise.

CORNELL UNIVERSITY, ITHACA, N. Y.,  
February, 1903.

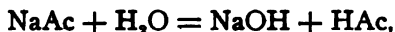
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## ON THE CLEANSING POWER OF SOAP.

BY H. W. HILLYER.

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CHEVREUL, the first to study the fats and soaps, discovered that when soaps are acted on by water they are hydrolyzed to free alkali and to an acid salt. The tendency of the reaction may be expressed by the equation



where Ac stands for the palmitic or stearic acid radical. The acid thus set free unites with more or less of the undecomposed soap to form difficultly soluble acid salts which contain more and more acid in proportion to the alkali as the dilution of the solutions from which the salts separate increases.

Rotondi, basing his conclusions on a mixed soap, decided that when water acts on the soaps, there is formed an acid salt which is soluble with difficulty in cold water and a basic salt which is easily soluble. Recent work by Krafft and his co-workers<sup>1</sup> have shown that Chevreul was correct and that Rotondi fell into error, prob-

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 1747; *Ibid.*, 27, 1755.

ably because he did not take into account the fact that sodium oleate is readily soluble in cold water. It was probably a mixture of this with the alkali set free by the hydrolysis of the palmitate and stearate present which was called an alkaline soap or basic salt. The more current theories of the detergent action of soap are largely based on the undoubted hydrolysis of soaps by much cold water.

The most ordinary theory is that the alkali set free by the hydrolysis of the soap acts on the fat to remove it by a process of saponification. To show that this is illogical it is only necessary to call attention to the fact that the alkali present has the opportunity of making a soap in either one of two ways: First, by acting on the glyceride to decompose it or, secondly, by acting on the fatty acid or acid salt from which it has just been separated. That it will more readily react with the latter than with the former is clear, and since, while the dilution is great, this reaction with the acid salt does not take place but rather the reverse reaction, it seems entirely improbable that the hydrolytic alkali acts chemically, if at all, on the glycerides of the fats and oils. In the use of soap for cleansing, we prefer to use hot and strong solutions but the hydrolysis is almost certainly more complete when the solutions are dilute and have cooled enough to yield a precipitate of acid salt. In the hot solution, especially if concentrated, there can be but little free alkali. Finally, paraffin oils are washed away by soaps as well as the glycerides are, and in this case it is clear that there can be no chemical reaction of the alkali upon the oil.

C. R. Alder Wright<sup>1</sup> assumes that the value of a soap is largely due to the alkali of hydrolysis acting in such a way as to allow contact of the water with the substance to be cleansed. Ladenburg's "*Handwörterbuch*," Vol. X, p. 574, favors the theory of Knapp, which lays the cleansing power of soap to the property of the soap itself of easily wetting oily substances. Knapp's original papers are not available to the writer and his evidence is not known, but it may be easily shown by a simple experiment that it is the soap itself and not the alkali which gives aqueous solutions the power of wetting oily substances.

A piece of red litmus paper is thoroughly oiled with either purified cottonseed-oil or a paraffin oil, and upon it is placed a

<sup>1</sup> Muir's "*Dictionary of Applied Chemistry*," Vol. III, p. 411.

drop of dilute alkali. The alkali produces a blue spot with well-defined edges, and spreads very slowly over the oiled paper. If a drop of soap solution is placed on the paper it spreads rapidly and soon produces a large spot with ill-defined ragged outlines.

Another suggestion as to the cleansing is that the soap itself or the alkali of hydrolysis acts as a lubricant, making the tissue and impurities less adhesive to one another, and in that way promoting the removal of the latter. It is not unreasonable to consider this as a factor in the cleansing, and it will be referred to again later.

It is often suggested, either as a distinct theory or as a more or less important adjunct to the saponification theory, that the alkali set free by hydrolysis acts on the fat by emulsifying it, and carrying it away in suspension with the other impurities. This suggestion has come apparently because those who have emulsified oils with alkali have used oils not free from fatty acids. It is also suggested that the emulsification is due to the undecomposed soap, but experiments are not recorded as far as can be ascertained to sustain this view or to determine whether the action is due to the soap or to the alkali.

When good cottonseed-oil, "salad oil," is shaken with weak alkali it is largely emulsified, but by washing the emulsion with water and dilute alkali alternately for many times, the soap formed by the action of the alkali on the free acid of the oil is removed, the oil separates from the emulsion, and a product is obtained which is not emulsified by decinormal sodium hydroxide. Neither is kerosene emulsified by decinormal alkali. Both kerosene and purified cottonseed-oil easily make permanent emulsions with a decinormal solution of sodium oleate. From this experiment, it seems certain that the emulsifying power of the soap solution, is due to the soap itself rather than to the hydrolytic alkali.

The explanation of the action of soap as due to its emulsifying power is a plausible one, but no clear account has been given, or made current, at least, in chemical literature, of the physical properties which a liquid must have to be a good emulsifying agent. The great similarity between foams and emulsions in method of making and in properties, suggests the question whether any explanation given for the formation and permanence of foams will not also apply to the formation and permanence of emulsions. Plateau and Quincke have made extensive studies of substances which foam and of those which are emulsifying agents.

There will be here no attempt to detail their results or to follow exactly their reasoning but the general trend of their work will be indicated. They have shown that soap solution has a surface-tension which is lower than that of any other aqueous solution. Its surface-tension is, in fact, only about 40 per cent. that of pure water. This may be shown in several ways. When two capillary tubes of the same diameter are placed respectively in water and in soap solution, the water will be seen to rise about 2.6 times as high as the soap solution. If a given volume of water is allowed to drop from a broad-ended pipette or stalagmometer and then a soap solution is allowed to drop from the same pipette, it will be found that the soap solution will make 2.6 times as many drops as the water. The cohesion of the soap solution is so small that the surface-tension will sustain drops of a volume only about 40 per cent. of the volume of those formed by water. Plateau<sup>1</sup> lays the power of forming bubbles, films, and foam to two factors: first, the liquid must possess notable viscosity, that the film may not readily yield to the forces which tend to thin it to the point of rupture; secondly, it must have a low surface-tension since the surface-tension is the most active force in thinning the film. Soap solutions are ordinarily quite viscous, and this viscosity is increased in Plateau's bubble mixture by adding glycerin, which aids in making bubbles and films permanent. Soap solutions have a low surface-tension and, on account of these two factors, soap solutions easily yield and enduringly maintain films and foam.

Quincke<sup>2</sup> has similar fundamental views, but ascribes the permanence of a foam to the mixed character of the liquid which foams, and claims that no pure liquid will foam. According to Quincke the permanence of the foam is due to the action of surface-tension which spreads out over the surface of the film some secondary ingredient of the solution, and this tends to close up any potential ruptures in the film. Plateau calls attention to the important part played by viscosity in these phenomena and speaks of the existence of a viscosity which pertains to the liquid itself, its internal viscosity, caused by the friction of the molecules of the liquid on each other and also of a second kind of viscosity, which he calls superficial viscosity, which sometimes makes the motion of a foreign body upon the surface

<sup>1</sup> Pogg. Ann., 141, 44.

<sup>2</sup> Wiedemann's Ann., 38, 592.

of a liquid more or, on the other hand, less ready than within the liquid. Stables and Wilson<sup>1</sup> have confirmed Plateau's work, and find that the motion of a body in the surface of a solution of saponin is resisted 600 times as much as it is within the same solution. By this great superficial viscosity they account for the great foaming power of saponin solution, although it has a comparatively high surface-tension.

To make these ideas clear a simple case may be used as an illustration. Suppose two bubbles of air to be lying side by side within a mass of water. The molecules of water at the point of nearest approach of the bubbles are acted on by the stress of the surface-tension of both bubbles, and this causes a thinning of the film between them. The surface-tension is great and the water is mobile so that the thinning will be rapid and soon the bubbles will coalesce by the breaking-down of the membrane. If, instead of water, soap solution is present, the stress which causes thinning will be less on account of the much smaller surface-tension and the resistance to thinning, due to the viscosity of the soap solution, will be somewhat greater and as a result the bubbles will remain separate for a much longer time. In the same way a mass of bubbles will remain permanent longer in soap solution than in water.

A table is here presented showing some observations made by the writer in confirmation of the work of Quincke and Plateau. While they claim no considerable accuracy, they show in general the tendency which solutions of high viscosity and low surface-tension have to make foams. The figures in the second column show the

	Time.	Drops.	Foam.
Water .....	3	47	—
Stale beer .....	..	79	+
Sweet skimmed milk .....	4	75	+
Saponin, 0.5 per cent .....	3	55	+
Albumen, 3 per cent .....	3	58	+
N/10 NaOH + equal volume alcohol .....	8	110	—
Glycerin, 50 per cent .....	14	60	—
Gum acacia, 6 per cent .....	8	49	—
N/10 rosin soap .....	3	104	+
N/10 sodium oleate .....	4	104	+
N/640 sodium oleate .....	3	108	little

number of minutes required for the volume of liquid contained in the stalagmometer to flow out and consequently give a rough measure of the internal viscosity of the solutions. The third

<sup>1</sup> *Phil. Mag.* (5), 18, 406.

column gives the number of drops formed from the given volume, when the drops were formed in air. In the fourth column the plus signs indicate that the solution makes a permanent foam and the minus signs that it does not. Water gives the smallest number of drops and has the highest surface-tension. The solution of sodium resinate and the solutions of sodium oleate give the greatest number of drops, and have the least surface-tension. That viscosity alone will not account for permanent foam formation is shown by the cases of glycerin and gum acacia where there is high viscosity but also high surface-tension and no foam. Beer and milk have a higher viscosity and a lower surface-tension than water and yield foams. The decided apparent exceptions are albumen and saponin, and alcoholic alkali. Saponin and albumen have, however, in a very marked degree, the property of superficial viscosity, and this accounts for the persistent foam in spite of their low internal viscosity and comparatively high surface-tension. On the other hand, while the solution of alkali in dilute alcohol has a high internal viscosity and a markedly low surface-tension, the temporary character of its foam may be accounted for by the fact discovered by Plateau—that alcohol has a negative superficial viscosity. That the alcohol has the effect of diminishing foaming power may be seen by adding a small quantity to a soap solution, which then loses its foaming power to a marked degree.

#### EMULSIONS.

Can emulsification be explained by the viscosity of the emulsifying agent? In the case of very thick liquids like the gum solutions used by the pharmacists, it is probable that the extreme viscosity is a very large factor in giving permanence to the separation of the oil droplets which have been formed mechanically. That even very large internal viscosity will not make an emulsion permanent is shown by the fact that 50 per cent. glycerin and 6 per cent. gum solutions which have viscosity of a high degree will not emulsify kerosene or even a viscous oil like cotton oil. Saponin or albumen solution with their high superficial viscosity will give permanent emulsions. Dilute soap solutions which have not great viscosity have very great emulsifying power, and the same is true to a less degree of some other solutions. From these facts it must be decided that internal viscosity of the liquid will not account for its emulsifying power.



It has been seen that foaming can be explained largely by the small surface-tension of soap solution towards air. Surface-tension phenomena show themselves between two liquids as well as between a liquid and air. The question arises whether there is any peculiarity in the degree of surface-tension between soap solutions and oils, not shown by other solutions.

Quincke<sup>1</sup> observes that when a solution of sodium carbonate is brought in contact with an ordinary oil, phenomena are exhibited which he ascribes to the change of surface-tension between the oil and aqueous solution on account of the formation of soap. Among the phenomena accounted for in this way is that of emulsification. Quincke does not use pure oils or single soaps nor, except casually, does he refer to the low surface-tension between oils and soap solutions.

To more definitely answer the question as to the relation of surface-tension and emulsifying power, experiments were made by the writer to measure roughly, by the dropping method, the relative surface-tension of water and of soap solution toward typical oils. According to Quincke a solution of Venice soap containing 1 part in 40 of water has toward air a surface-tension of 2.563, a solution of 1 part in 400 has a surface-tension of 2.672, and one of 1 part in 4000 has a surface-tension of 2.681. In other words, according to these careful determinations, concentration has very little influence on the surface-tension of soap solution in contact with air. With this constant and comparatively small reduction of surface-tension which soap solution shows as contrasted with water, it is interesting to compare the enormous and variable reduction of surface-tension shown when soap solutions of increasingly concentration are allowed to flow through oils.

When cottonseed-oil is allowed to flow slowly up through water, it makes much larger drops than are made when it flows up through soap solution. The same is true when kerosene is used. The surface-tension between the oils and soap is much less than between the oils and water. A much more convenient method of studying the surface-tension is to let the water or solutions flow down through the oils. In this work the greater number of observations were made with a stalagmometer intended as an alcoholimeter and holding 5.35 cc.

When water flows from a stalagmometer with its tip immersed

<sup>1</sup> Wiedemann's *Ann.*, 35, 580.

in oil, large drops are formed. When a weak soap solution replaces the water, the drops are smaller. When stronger and stronger soap solutions are used, the drops grow smaller and more rapid, if the rate of flow of the liquid is not checked, until with a strong solution the rate of flow is too rapid to give time for the formation of separate drops and a very thin cylindrical stream flows from the stalagmometer. The surface-tension has become so small that it does not support the liquid long enough to form drops. In this case, gravity is strong enough to almost completely overcome the action of surface-tension and draws the solution out into a fine thread. It seems reasonable to suppose that any other outside force could easily break up this strong soap solution within the oil into small droplets, or spread it into films on account of the small surface-tension. According to the theory of surface-tension between two liquids, surface-tension will be great between them, when each liquid has strong internal attractive forces, that is, strong cohesion; and it will be small when they have slight attraction for one another, that is, slight adhesion or mutual affinity. Small surface-tension will be caused by a weak cohesion of at least one of the liquids and a strong adhesion or affinity of the liquids to one another. Water forms large drops in oil on account of its great cohesion and its small adhesion to the oil. Soap solution makes small drops or runs down in a stream; because, first it has a low cohesion and, secondly, because it has a strong adhesion to the oil or a strong affinity or attraction for it.

It would seem that this low surface-tension of soap solutions must be a prime factor in their emulsifying power. Viscosity can have very little to do with it, for solutions containing about 1 per cent. of sodium oleate are excellent emulsifying agents but have a viscosity so low that careful measurements would be necessary to show that they are more viscous than water. Using the same reasoning as in the case of bubbles and foam, we may say that when two oil drops approach each other in water, they tend to coalesce and finally do so because the great surface-tension of the drops easily withdraws the mobile water from between them till they touch and coalesce. But when the drops are in soap solution, the surface-tension is so very much less that it is not able to withdraw the solution rapidly from between the drops, and they are kept separate. If the soap solution is notably viscous, the slight surface-tension will have still greater difficulty in thinning the

films to the point of rupture. A mass of droplets separated by films of a low surface-tension and notable viscosity will be a permanent emulsion.

Quantitative relations between the surface-tensions of certain solutions are given in the following table. The measurements are only approximate, but, for the purpose, adequate. The first column (K) indicates the number of drops formed when 5.35 cc. of the solutions named flow into a certain kerosene. The second column (Emul. K) indicates by a plus sign, that the solution, when shaken with the kerosene, will yield an emulsion. The third and fourth columns, C.S. oil and Emul. oil, give similar data for cottonseed-oil carefully purified from free acid by washing with dilute alkali.

	K.	Emul. K.	C.S. oil.	Emul. O
Water .....	17	—	9	—
Stale beer .....	39	little	..	—
Sweet skimmed milk .....	..	..	52	+
Saponin .....	..	..	13	+
Acacia .....	..	..	14	+
Alcohol and sodium hydroxide .....	51	little	..	..
N/640 sodium oleate .....	26	little	..	..
N/10 sodium oleate .....	296	+	167	+
N/10 rosin soap .....	310	+	180	+
N/10 sodium chloride .....	17	—	..	..
N/10 sodium hydroxide .....	17	—	10	—
Sodium silicate .....	..	..	15	—

From these data, it will be seen that the solutions which emulsify have a larger number of drops, that is, "a smaller surface-tension than those that do not."

Saponin solution containing 1 part of the glucoside to 200 of water is an excellent emulsifying agent, and yet its surface-tension toward oil is not enormously reduced from that of water, but its emulsifying power is easily understood when one observes the form of the drops produced when it flows through cottonseed-oil. Quincke has observed similar drops when albumen solution flows through oil. We may make a *soap* solution, one containing 1 part of sodium oleate in about 500 parts of water, which, when it flows through oil, will give the same number of drops as the saponin solution used. The drops of soap solution form normally, and, as they fall, assume quickly a spheroidal shape, while the halving drop quickly takes the form of a catenoid. A drop of

saponin solution (Fig. 1) as it is detached takes the form of a Rupert drop (*a*) and, falling to the bottom, takes the form of a pear (*b*) with the stem plainly visible. This stem, the remains of the filament drawn out as the drop was detached, may remain

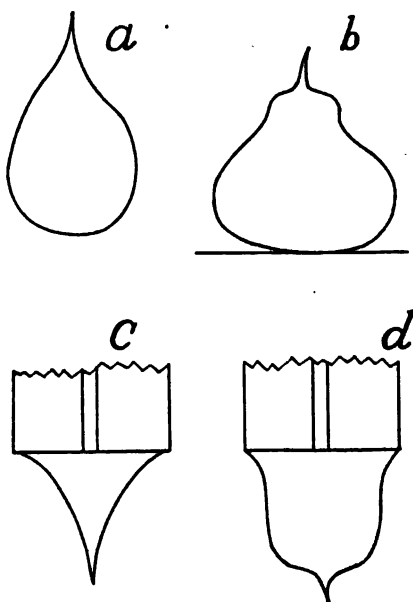


Fig. 1.

visible for many minutes. The hanging drop, if the flow of solution is stopped just after the fall of the drop, has the shape of an inverted cone, with incurved sides and a slender peak (*c*). This shape is retained a long time. When new liquid flows in, the hanging drop changes its shape only as its surface is swelled out by the inflowing liquid (*d*). That the liquid is not in itself viscous may be known by observing the ready rotations and other movements of chance particles within the drop as the liquid flows down.

Here we plainly have a new instance of superficial viscosity, a viscosity which makes motion difficult in the surface between the two liquids. This it would seem, being of so considerable a degree, may account for the resistance offered to the withdrawal of the films of saponin from between the oil droplets of a saponin oil emulsion, and consequently for the permanence of the emulsion.

The conclusion arrived at is that emulsincation is due largely to the small surface-tension between oil and the emulsifying agent which allows the emulsifying agent to be spread out into thin films, separating the oil droplets. The surface-tension is not strong enough to withdraw the film from between the droplets except slowly and, if the emulsifying agent has great internal viscosity, or if great superficial viscosity is shown between the liquids, the thinning of the film becomes so slow that the emulsion is permanent.

#### EFFECT OF FREE ALKALI AND OF FREE ACID.

As indicated in the tables last given, decinormal sodium-hydroxide solution does not show any greater number of drops than water when it flows through kerosene, and only a slight, and in this connection insignificant, increase in the case of cottonseed-oil. Since alkali does not emulsify either of these oils, we may conclude that diminution of surface-tension and emulsifying power go together, and that neither of them is caused by alkali alone. Solutions of alkali less concentrated than decinormal also show the same surface-tension and fail to give emulsions. A decinormal solution of sodium oleate will give some twenty times as many drops as a decinormal alkali. The number of drops formed by the oleate is not increased by adding excess of alkali to either concentrated or dilute solutions of oleate. On the other hand, when free oleic acid in excess is added in increasing amounts to a decinormal solution of sodium oleate, the number of drops and consequent emulsifying power are decreased as shown by the data and curve below. Mixtures were made containing 100 cc. oleate and amounts of free oleic acid varying from an amount sufficient to form the acid salt  $C_{18}H_{34}O_2Na:C_{18}H_{34}O_2$ , down to  $1/128$  of that amount, and the number of drops which each made was determined.

#### DECINORMAL SODIUM OLEATE AND OLEIC ACID.

Equivalents of oleic acid in excess.	0.	$1/128$ .	$1/64$ .	$1/32$ .	$1/16$ .	$1/8$ .	$1/4$ .	$1/2$ .	1.
No. drops .....	274	273	270	240	216	164	117	84	58

From these facts we may conclude that the low surface-tension and the emulsifying power are due not to the alkali or to the acid salt set free by the hydrolysis but to the *undecomposed soap itself*.

We have seen before that another possible factor in cleansing,

namely, the power which soap solutions have of wetting oily substances is due to the soap itself. But this wetting power may be

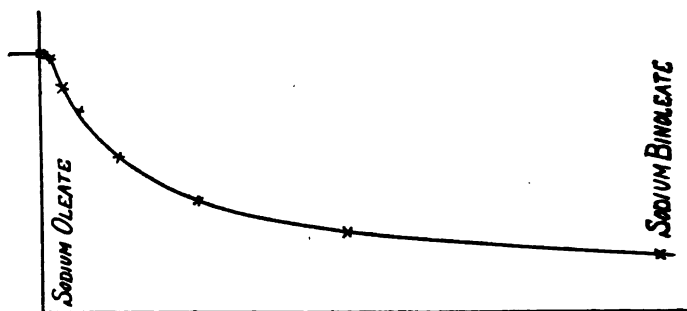


Fig. 2.

explained also by the strong adhesion of the soap to the oil and the low cohesion of the soap solution itself. The latter will more easily be spread out over the surface, if its cohesion is small and a stronger force will be acting to spread it out, if it is strongly attracted to the oily surface.

A very similar factor in cleansing is that which may be called ease of penetration, by which the aqueous solution pushes into and permeates the interstices of the fabric. If a glass tube of 3 or 4 mm. internal diameter and closed at one end is filled with cotton-seed-oil and immersed in a vessel of water (Fig. 3, *a*), the oil will not leave the tube, being held there by the strong surface-tension film between the oil and water. But if a strong solution of soap is poured in, the surface-tension film is diminished in strength, the oil flows from the tube, and the soap solution penetrates into it (Fig. 3, *b*). Here the soap, on account of its weak cohesion and its strong adhesion to the oil, withdraws the oil and penetrates into the oily tube. In the same way, it may be, the soap penetrates into the capillary interstices of the fabric to be cleansed.

Even the lubricating power of soap solutions may be explained by considering the factors a low cohesion and a strong adhesion. In treatises on mechanical engineering, the chief physical property mentioned as desirable in a lubricant is that it shall have

sufficient "body" or viscosity to prevent its being pressed out from between the surfaces to be lubricated. While viscosity is for this particular object no doubt a necessary thing, it would seem to be a necessary evil. As the term is used in physics, viscosity is a property of fluids which pre-

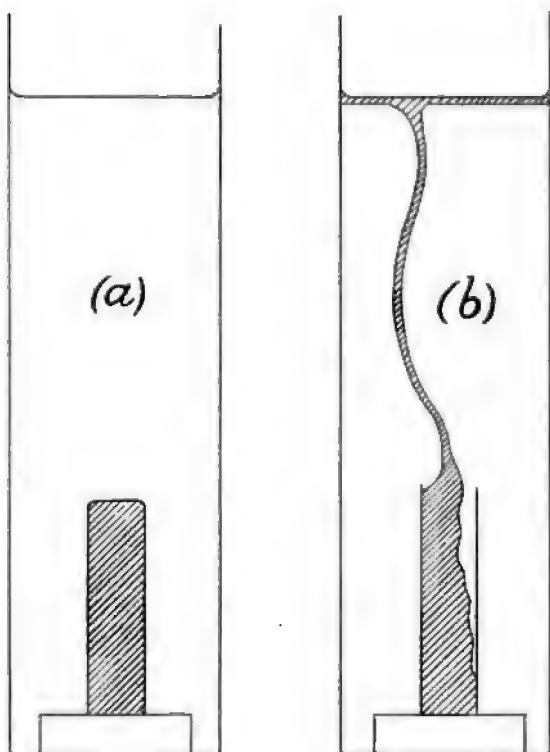


Fig. 3.

vents the freedom of motion which their particles would have if the fluid had no viscosity, or a less viscosity. But in speaking of lubricants mechanical engineers demand, in a substance intended to promote motion, a property which physically hinders motion. If we consider as lubricants graphite or steatite or soap, or the clay on which our shoes slip in the street, we may get a clearer notion of lubrication. In these cases, at least, the lubrication is due to the fact that the lubricant adheres in a film to the surfaces

to be lubricated but does not cohere to itself. In the use of oil as a lubricant, it is also true that the oil adheres to the lubricated surfaces and soon forms two layers of oil which glide over one another. We have then strong adhesion on the part of lubricant and a weak cohesion. The same is true of soap solutions and will explain their slipperiness and lubricating power. The slipperiness we feel when alkali is used on the hands is probably due to its action on the skin or on the material which keeps in place the epithelial cells. The actual removal of these cells with the impurities attached to them and covered by them would account for the cleansing action of alkali and alkali carbonate on the skin.

The position here taken is then : that the cleansing power of soap is largely or entirely to be explained by the power which it has of emulsifying oily substances ; of wetting and penetrating into oily textures ; and of lubricating texture and impurities so that they may be removed easily. It is thought that all of these properties may be explained by taking into account the low cohesion of the soap solutions and their strong attraction, adhesion or affinity to oily matter, which together cause the low surface-tension between soap solution and oil.

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## A STUDY OF SOAP SOLUTIONS.

BY H. W. HILLYER.

Received March 20, 1907.

It was noted in the preceding article that while toward air the surface-tensions of soap solutions vary but little as the concentration is changed, the surface-tension between soap solutions and oils is rapidly diminished as the concentration is increased. To ascertain the law connecting concentration and surface-tension, the following experiments were made. They not only show this relation but serve to confirm the idea that the diminution of surface-tension is dependent solely on the amount of undecomposed soap present in the solution. Unfortunately in this pioneer work it was not realized how desirable it was to have the same kerosene for all experiments, and consequently the results are not strictly



and numerically comparable except in the cases which are plotted together. But it is thought best at this time to publish these results, as their general tendency is quite clear and as they serve to indicate the basis on which rests the method for evaluating soaps which will soon be published.

A decinormal solution of sodium oleate was prepared by dissolving 14.1 grams of oleic acid in 500 cc. decinormal sodium hydroxide solution. The solution was almost completely clear. It was then filtered. The solution was diluted successively to lower concentrations and the number of drops formed when these various solutions were passed through kerosene was noted. Duplicate counts were made and the number of drops found in the separate counts are indicated.

## SODIUM OLEATE.

Concentration.	N/10.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	Water.
No. drops .....	{ 464	269	184	116	80	51	35	20
	{ 460	270	181	116	78	54	35	20
Another set of solutions...	..	292	184	118	74	49	32	..
				124	77	47	31	..

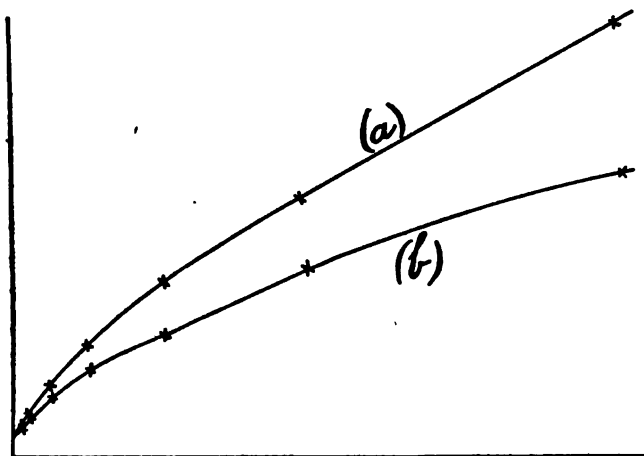


Fig. 1.

In the diagram (Fig. 1, *a*) the ordinates show the number of drops formed and the abscissas show the concentrations. The number of drops is not proportional to the concentration but falls

below proportionality as the concentration increases. In another experiment, the solutions were very carefully made and after preparation were placed in stoppered flasks in a large tank of water that they might be kept as nearly as possible at an average room temperature. The special object of this experiment was to ascertain whether any change took place on standing which would indicate that a hydrolysis of the soap was gradually going on. In this case the kerosene was the same throughout the experiment, but different from that used in the last. For each count the kerosene was changed except where the solutions were very dilute. The solutions of various concentration were prepared as rapidly as possible and then the counts made. After this the solutions were kept at the temperature of the tank of water and the counts repeated from day to day.

#### SODIUM OLEATE, TIME AND DILUTION.

Concentration.	N/10.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	Water.
December 2nd .....	297	196	125	88	63	41	26½	14
December 3rd .....	296	200	126	87	61	40½	26½	14
December 5th .....	..	194	123	85	62	40½	26½	..
December 8th .....	301	..	132	..	59½	..	26½	..

From this it seems that in the course of six days no change takes place in the surface-tension. There is no evidence of any decomposition of the soap by a diminution of the number of drops in either strong or dilute solutions. The curve (Fig. 1, *b*) showing the relation of concentration to number of drops is here shown in connection with that given above that it may be seen that the two have the same shape. They should not, however, be compared numerically except to enforce the fact that the effects are quite different with different samples of kerosene. When sodium oleate solutions stand in uncorked flasks, the carbon dioxide of the air decomposes the soap and the number of drops formed by a given solution gradually diminishes. This is especially marked in case of dilute solutions.

#### SODIUM PALMITATE AND STEARATE.

Pure sodium palmitate and stearate are very little soluble in cold water, so little in fact that it is difficult by shaking them with

cold water to produce a foam. Palmitate and stearate, when rubbed on the hands with cold distilled water, do not give the effect of soap but seem more nearly like paraffin or tallow. On account of this small solubility in cold water, it was necessary to devise a method of working at a higher temperature. The apparatus finally used is very simple. It consists of a beaker of about 700 cc. capacity provided with a cover of zinc with its edges turned down. In the cover are three holes one for the thermometer and two large enough to receive short wide test-tubes. One of the test-tubes serves as a reservoir to hold the hot soap solution to be used, while the other is the working part of the apparatus. After the water in the beaker has been heated to boiling, a supply of the solution to be tested, which has been heated to bring the soap into solution, is placed in the reservoir tube. Then 15 cc. of kerosene are placed in the working tube and the pipette put in. When all is thoroughly heated to the boiling temperature, the pipette is filled with the solution, placed with its end below the oil and the number of drops counted. At first, great difficulty was

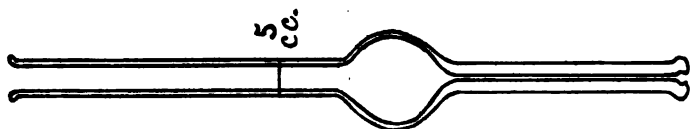


Fig. 2.

encountered in getting concordant results but it was learned that when the lower end of the pipette was *ground* off the numerous minor capillary tubes in the glass of the lower part of the pipette continually gave out small amounts of air and when this formed into bubbles on the end of the pipette it caused an increase in the number and decrease in the size of the drops which were forming. As this exudation of air was irregular and introduced a new factor in the surface-tension problem a means was necessary to prevent it. The remedy was to so shape the pipette that the lower end after grinding could be heated to the point of fusion until all the small capillaries were closed without closing the main capillary or narrowing too much the surface on which the drops were to form. The form finally worked out is shown in the accompanying sketch (Fig. 2).

Twentieth-normal sodium palmitate was made by treating 12.8 grams palmitic acid with 500 cc. decinormal sodium hydroxide and 500 cc. water, and heating all on the water-bath. The solution was quite clear. Small quantities of palmitic acid were added until oil droplets were plainly visible and the solution was filtered. This solution was then diluted with hot water to make the concentrations used below and these were kept on the steam-bath at 60°-70°. None of them were more than slightly cloudy at 60°-70°. They were tested in the apparatus just described, and gave the number of drops here set down.

SODIUM PALMITATE.							
Concentration.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
No. drops .....	{ 424	315	223	94	49	32	23
	..	..	226	88	49	33	23½

On plotting these data, the curve (Fig. 3, a) results. The sag

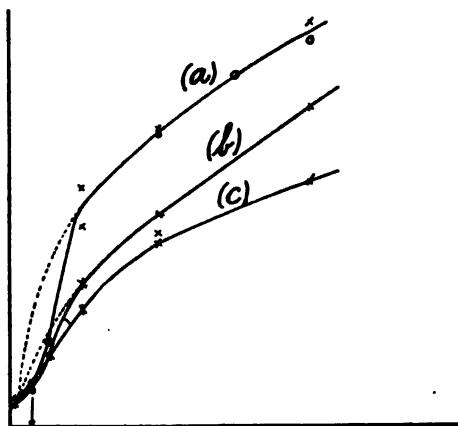


Fig. 3.

in the curve near its origin was thought so remarkable that a second set of solutions was prepared and tested.

N/20.	N/30.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
403	368	308	208	90	40	31	24

When these data are plotted, a curve is obtained in shape like that obtained before and practically identical with it. If the same law connected concentration with the number of drops at low as at high concentration, the curve would be a smooth one extending to the point showing the number of drops made by water, as indicated by the dotted line. That the curve falls below

this line may be explained by supposing that in the dilute solutions a marked hydrolysis takes place. Krafft and Stern found that it was necessary to dilute a solution of sodium palmitate till it contained only about 1 part in 1000 before the precipitate formed on cooling had the composition of the true acid salt,  $C_{16}H_{31}O_2Na$ ,  $C_{16}H_{31}O_2$ . It is to be noted that the greatest depression in the curve above is in the region where the concentration is near to 1 part in 1000 of water. This point is marked by the arrow. If this is a true explanation, it is an interesting confirmation of the supposition that the number of drops is a function of the amount of undecomposed soap present. The hydrolysis lessens the amount of soap, and farther, the acid salt may in this case, as in the case of sodium oleate, actually diminish the number of drops which would be formed if the soap were alone. It would seem that we have here a proof that actual hydrolysis takes place while all of the substances are in solution. At the temperature at which the work was done the solutions are quite clear and show no sign of a precipitate.

#### SODIUM STEARATE.

Sodium stearate solution (one-twentieth normal) was made by dissolving 2.84 grams chemically pure stearic acid in 100 cc. hot decinormal sodium hydroxide solution and diluting to 200 cc. with hot water. The dilute solutions were made as before and the number of drops made by each determined at 100°. None of the solutions at 100° show more than a very slight opalescence. The number of drops formed are shown in the table:

#### SODIUM STEARATE.

N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
328	213	143	} 72 {	38	31	29
340	228	149		40	28	33

The curve (Fig. 6, b) showing these numbers in a graphic way has very much the same shape as that for sodium palmitate and here also the greatest hydrolysis is apparently at a point where there is present about 1 part of the salt to 1000 of water. By comparing the shape of these curves with that of sodium oleate at 100° it becomes evident that their peculiar form is not due to the action of the higher temperature. As a passing observation it may be noted that when the solutions stand in the cold, the precipitates formed in the N/160 solution and those of greater con-

centration, float in the solutions, while the precipitates formed in the N/320 solution and those of less concentration sink in the solutions, this change of relative density also taking place when the solution contains about 1 part of sodium stearate in 1000 of water.

#### SODIUM OLEATE AT 100°.

Sodium oleate solutions when tested at 100° show no special change in the form of the curve connecting concentration and number of drops from that belonging to the oleate in the cold. Since the data were obtained using the same apparatus and same kerosene as that used for the palmitate and stearate they are plotted in the same diagram at *c* (Fig. 3).

#### ROSIN SOAP.

The soap made by action of alkalis on colophony is so common a constituent of yellow soaps that a study of its solutions is of some interest, especially if we may gain knowledge of the reason of the disfavor with which the soap is regarded. A solution of rosin soap approximately decinormal was prepared by digesting in the cold powdered rosin in excess with decinormal sodium hydroxide solution as long as any rosin was dissolved. This solution was diluted with freshly boiled cold water to give the concentrations indicated below and each tested in the cold to learn the number of drops made by each.

#### ROSIN SOAP IN THE COLD.

Concentration.	N/10.	N/20.	N/30.	N/40.	N/60.	N/80.	N/160.	N/320.	N/640.
No. drops .....	361	236	201	151	118	78	47	32	26
	353	243	207	155	123	79	46	34	25

These results are plotted in curve *a* (Fig. 4). The same solutions were tested at 100°, using the same pipette and same kerosene.

#### ROSIN SOAP AT 100°.

Concentration.	N/10.	N/20.	N/30.	N/40.	N/60.	N/80.	N/320.	N/640.
No. drops .....	288	215	183	123	68	45	35	29
	289	215	187	127	67	45	35	28

These results are plotted in curve *b* (Fig. 4). The notable thing in both curves is the sag near the origin. The more dilute solutions give a smaller number of drops than might be expected if the same law held that governs with higher concentrations. If, as is indicated by the facts given in this and the preceding paper, the number of drops is a measure of the amount of undecomposed

soap present in solution, it seems that with the rosin soap as with the palmitate and stearate a marked hydrolysis takes place in dilute solutions. The solutions with the exception of the decinormal

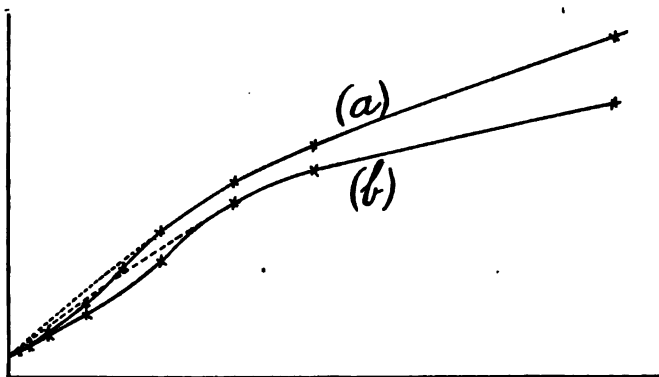


Fig. 4.

and one-twentieth normal are much clouded, even in the cold, showing by this also that hydrolysis has taken place. The hot solutions, even the most concentrated, are cloudy. The hydrolysis indicated by this cloudiness is also shown by the fact that the curve for the hot solutions lies below that for the cold solutions. Elevation of temperature is favorable to diminution of surface-tension and a greater number of drops might be expected with all these solutions at the higher temperature but, as a smaller number is found, the explanation lies in the hydrolysis caused by heating the solutions.

In looking over the results obtained, it is of interest to note their agreement with well-known facts in regard to the soaps. The oleate is very soluble in cold water and even in dilute solutions shows little hydrolysis. Soaps rich in oleate are useful for toilet purposes and for wool-scouring when cold water is used. Its stability in dilute solutions would make it of value as a detergent even until it is completely rinsed away and its ready solubility would make it easy to wash away.

For laundry work, dish-washing, and other work, when hot water is used, practical experience shows that the most desirable soap is a tallow soap. This is rich in palmitate and stearate with some oleate. As shown by the curves, the palmitate and stearate have a very high efficiency at a high temperature, especially when the concen-

tration is great. When the concentration is lessened, marked hydrolysis takes place and the efficiency rapidly falls off, but with mixed soaps this low efficiency of the palmitate and stearate is supplemented by the relatively high efficiency of the oleate in dilute solutions, which will sustain the detergent effect until all impurities are washed away, including the acid palmitate and stearate which might otherwise be retained by the fabric. When the temperature is low, palmitate and stearate are so little soluble as to be of no practical value, since the only effect of water on them is to hydrolyze them and set free a small quantity of alkali which, according to the hypothesis here favored, has no detergent effect on neutral oils.

Rosin soap is usually regarded as a comparatively undesirable ingredient of soaps. By a test with decinormal solution, it is of about the same efficiency according to the dropping test in kerosene as sodium oleate. But when the dilution curves are studied, it is seen that dilute solutions, especially in the heat, show marked hydrolysis which is necessarily accompanied by separation of the rosin acids. Here the acid product of hydrolysis separates in a cloud and does not stay in solution as with the palmitate and stearate in the heat. The separated rosin acids may well settle on the fabric being washed and impart to it the odor of rosin, cause it to be yellow and make it ready to easily take up dust. This effect may be partially offset in using mixed soaps, by the other ingredients whose detergent action will tend to remove the rosin acids, but the evil effect will still, to some extent, remain.

In this work, when kerosene is used as the test substance, it is, of course, true that we are really measuring the detergent effect of the various soaps toward kerosene only. Some few observations show that toward other fats and oils the relative efficiency of the different soaps is different. It may be necessary to take this into account when judging the value of a soap for some special purpose.

LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY  
OF WISCONSIN, March 17, 1902.

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#### NOTES.

*Note on the Bromination of Heptane.*—Venable<sup>1</sup> found that the bromination of normal heptane from the *Pinus Sabiniana* yielded

<sup>1</sup> *Am. Chem. J.*, 10, 237.



a mixture of bromides which varied in amount with the temperature and the time. Theoretical amounts of heptane and bromine were used but a large percentage of heptane was unattacked in every case. The secondary heptyl bromide was the main product when the heptane was kept boiling, and the bromine was added during a course of five hours, which was as rapidly as the bromine was taken up. The yield was 30 per cent. of the theory. This bromide is best obtained from heptane of the *Pinus Sabimiana* of California which was formerly on the market under the name "abietine," a patent remedy. Small quantities only can now be obtained under great difficulties, as Blasdale<sup>1</sup> reports. The stock on hand in our laboratory is small and hence valuable. In view of this I thought it possible to increase the yield of the secondary bromide by carrying out the reaction under increased pressure. By means of air-pressure the liquid bromine was forced into the flask containing the boiling heptane. A compact reflux condenser within the neck of the flask completely condensed the heptane. A side tube of the condenser led into a long glass jar, set horizontally, filled with stick potash to absorb the hydrobromic acid evolved. To the further end of the jar was fitted a tube which, entering a jar of mercury vertically, opened at a point 190 mm. below the surface. Several attempts were made to increase the yield of the secondary bromide with this apparatus but without success. I wish here to express my thanks to Mr. M. R. Glenn for his kind assistance in this work.

I then turned my attention to the possibility of accomplishing the result by employing an excess of bromine. The method employed by Venable was followed. Where he used 180 grams bromine for 100 grams heptane I used 240 grams bromine. The table shows the results after six complete fractionations, the first two being under diminished pressure.

		Theoretical amount of bromine. Grams.	Excess of bromine. Grams.
I.....	100°-120°	30	8
II.....	120°-162°	6	2
III.....	162°-168°	55	65
IV.....	168°-173°	2	1.5
V.....	173°-183°	8	2
VI.....	183°-210°	10	45

I consists principally of unattacked heptane and III of the

<sup>1</sup> This Journal, 23, 162.

secondary heptyl bromide. The excess of bromine, then, considerably diminishes the amount of unchanged heptane; increases the secondary bromide by 18 per cent. but causes a much greater increase in the bromides of higher boiling-points. A further consideration of the table shows that 22 grams less of heptane are recovered, but as a compensation there is a gain of 10 grams of the secondary bromide. Now if 22 grams of the heptane were treated with the theoretical amount of bromine only 6.6 grams of this bromide would be obtained. Hence there is actually a net gain in the yield of the secondary bromide as well as a reasonably good gain in time. The process is a very long one and these gains are worth consideration.

ALVIN S. WHEELER.

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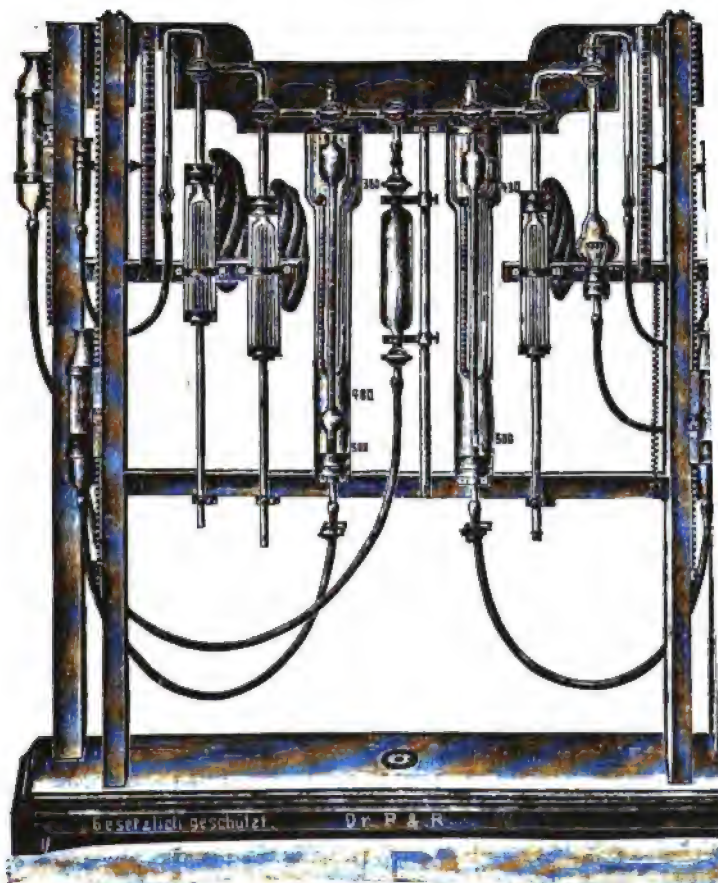
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*New Apparatus for the Examination of Choke-damp and Nitrogenous Mine Inflammatory Gases.*—The apparatus is composed of two burettes which are connected with a 3-way stop-cock capillary, and this with the gas-bottle for filling the burettes. Both burettes are filled at the same time with the gas which is to be examined, and this makes it possible for the apparatus to give an exact determination of oxygen, methane, and carbon dioxide. On the right side, at first, carbon dioxide is absorbed in the caustic potash receiver and then methane is burned in the pear-shaped receiver by a platinum spiral which is glowing from an accumulator.

During the absorption of the carbon dioxide and the cooling of the pear, the oxygen is determined on the left side, so that a complete choke-damp examination of methane, carbon dioxide and oxygen is finished in about twenty-five minutes.

The fluctuation of the temperature which has occurred during the examination of the gas is found on a special thermometer, divided in  $1/10^{\circ}$  C., and arranged in the cooling-receiver; the variation of the volume of the gas brought about by the fluctuation of the temperature is equalized by the lifting and sinking of the manometer-receivers on each side. The gas is put into the burettes by means of mercury and can be read from the mercury. The apparatus is very sensitive and works exactly to 0.05 per cent. The apparatus solves the problem of the examination of choke-damp in

# NOTES.



the simplest, quickest and most exact manner according to Sect 71 and 72 of the general mining police order, January 18, 1901 the Royal Head Mining Office, Breslau. The apparatus serves further for the determination of methane in the high nitrogen gases which are found in mine inflammatory gases. It is quick and accurate for determining their content of carbon monoxide.

F. SCHREIBE

*A Burette and Standard Solutions Convenient for the Determination of Nitrogen by the Kjeldahl Method.*—By using the burette described below together with the standard solutions of strength recommended, all calculations and use of tables can

avoided. One gram of material is used and the standard solutions for titrating are N/2 sulphuric or hydrochloric acid and N/14.04 alkali. One cc. of alkali of this strength will be equivalent to one milligram of nitrogen and 1 cc. of the N/2 acid will be equivalent to 7.02 cc. of the alkali.

The burette used is an ordinary 100 cc. burette with side inlet at the base, graduated to 1/10 cc., and having the figures running up, instead of down, the graduation; that is, 0 is at the base of the burette and 100 at the top.

For the determination, 8 cc. of the N/2 acid are run into the receiver, the distillation made and the distillate titrated with the N/14.04 alkali in the following manner. The alkali is run into the burette from the stock bottle until it reaches 56.16. The titration is now made and the reading of the burette at the end is the per cent. of nitrogen multiplied by 10. This is seen from the following reasoning.

As 1 cc. of the N/2 acid is equivalent to 7.02 cc. of the N/14.04 alkali, 8 cc. will be equivalent to 56.16 mg. of nitrogen. As the titration was started with the burette reading at 56.16 and run down until the neutral point was reached, the alkali remaining in the burette must be equivalent to that which was in the distillate. The reading of the burette then gives the milligrams of nitrogen in the distillate. This divided by 10 gives the per cent.

In this laboratory N/2 sulphuric acid and N/14.04 ammonia are used. The ammonia will keep at least four months without any perceptible change. If the reagents used give nitrogen in a blank determination, subtract the reading of the blank from the burette reading. If the substance examined contains over 5 per cent. of nitrogen, use 0.5 gram for the determination, multiplying the result by 2, or increase the amount of N/2 acid used to collect the distillate, remembering that for every additional cubic centimeter of the standard acid used the reading of the alkali in the burette must be increased 7.02. For 8 cc. the burette is filled to 56.16; for 10 cc., 70.2; for 12 cc., 84.24.

In this laboratory the following number of cubic centimeters of the solution are used for the determinations indicated.

	Acid. cc.	Alkali. cc.
Total nitrogen .....	8 equivalent to 56.16	
Ulsch-Street (nitrates) .....	6     "     "	42.12
Magnesium oxide (free ammonia) .....	4     "     "	28.08

Instead of the 100 cc. burette mentioned above, one, two or three automatic burettes may be used; one constructed to automatically fill itself to 28.08 cc., one to 42.12, and one to 56.16 cc. These should be graduated to 1/10 cc. and the figures should run up the burette as in the one described above. Burettes of this kind can be obtained of Richards & Co., of New York.

LABORATORY OF THE AGRICULTURAL EXPERIMENT STATION OF THE R. I. COLL. OF A. AND M. ARTS.

A. W. BOSWORTH.

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*Note on Perkin's Test for Bicarbonates.*—There was recently published,<sup>1</sup> by F. M. Perkin, a test for bicarbonates based on the fact that bromine is liberated in a mixture of solutions of a bromide and sodium hypochlorite, if a dilute acid is added. Bicarbonates are sufficiently acid to bring about this reaction and may thus be distinguished from normal carbonates.

This test has proved very satisfactory in practice but the following exceptions must be noted: The test will not show the presence of ammonium bicarbonate nor can ammonium bromide be substituted for the sodium or potassium salts. Further than this, the presence of ammonium salts, even in very small quantities, prevents the reaction entirely. The ammonium salts experimented with were the chloride, carbonate, nitrate, sulphate, and oxalate, using solutions of the usual reagent strength and 5 per cent. solutions of sodium bicarbonate and potassium bromide.

For the test, 1 cc. each of the bromide and hypochlorite solutions were used and 10 or 12 drops of the bicarbonate solution. Of the interfering ammonium salt solution, 2 drops, added before the bicarbonate, absolutely prevented the liberation of bromine, except in case of the oxalate, and a small additional quantity of this produced the same result.

Incidentally it may also be remarked that care must be taken that the hypochlorite solution used is reasonably fresh and has been kept away from light, or it will be sufficiently acid to lead to erroneous results.

FRANCIS O. TAYLOR.

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*A Convenient Form of Table for Calculations of Chemical Weights.*—The author, having frequent occasion to check calculations of weights of substances made by students in quantitative analysis, has constructed a table, to enable him to quickly obtain

<sup>1</sup> *J. Soc. Chem. Ind.*, 22, 1375 (1902).

such results. This is presented to the Section as an accessory in teaching which may prove instructive to the pupil and helpful to the teacher, and in a measure replace the use of the "rechentafeln" often so employed.

Upon coordinate paper, 500 by 400 mm., the abscissa 500 mm. is taken as 1000, and there is laid off upon the vertical ordinate, the length corresponding to the ratio for reduction of weight sought for weight found. A straight line is then drawn from the origin to this point. Thus we take for the copper in cupric oxide 798 or for chlorine in silver chloride 247.

A diagonal line is thus drawn from the origin for each such ratio to be employed. We then read off upon the horizontal abscissa the measure corresponding to the figures of the weight found and the length of the ordinate at that point, cut off by the diagonal line for that substance, gives directly the amount of the body sought.

F. P. DUNNINGTON.

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### NEW BOOKS.

PRINCIPLES OF INORGANIC CHEMISTRY. BY HARRY C. JONES. New York: The Macmillan Co. 1903. xx + 521 pp. Price, \$4.00.

"The aim of this book is to add to the older generalizations those recently discovered, and to apply them to the phenomena of inorganic chemistry in such a way that they may form an integral part of the subject, and, at the same time, be intelligible to the student" (*Preface*).

The author states in the preface that the work is intended primarily for use by students of qualitative and quantitative analysis, and it may be presumed therefore that its aim is to modernize and expand the views of those who have already received some instruction in the elements of the science. At this stage, occasions for the application of modern ideas connected with ionization, mass action, solubility, and solution tension are certainly innumerable. Every operation in analysis, even the most trivial, bristles with opportunities for the use of these conceptions and can be performed intelligently and with unflinching success only by a student alive to the situation.

The book covers the general ground of a text-book of inorganic chemistry, but the theory of ionization and its application to the

explanation of chemical changes, including many of those used in analysis, receive special attention. Mass action, the phase rule, and Nernst's theory of solution tension, as well as radioactivity, colloidal solutions of metals, and other topics of contemporary interest are also discussed. Noteworthy features, besides the numerous ionic explanations of reactions, are the solubility curves of salts and the frequent tables showing the degree of ionization of various substances. The student whose training in general chemistry has lacked illumination by modern views, whether on account of the ignorance, conservatism, or deliberate preference of his first instructor, will find in this book abundant opportunity for bringing his conceptions up to date and getting in touch with the science as it is. To such a student the book will be most suggestive and stimulating. Dr. Jones is to be congratulated on having produced one of the best of the recent attempts to apply physico-chemical conceptions to undergraduate instruction.

The task essayed by the author is a difficult one, however, and the present volume is only a contribution towards the solution of the problem and not the solution itself. The treatment is one-sided. Ionic explanations abound, but chemical equilibrium which is fundamental to the understanding of ionic explanations in anything but a superficial way, and is of universal application outside of this restricted area, receives scant notice. The discussion of this subject is cut up awkwardly (*cf.* pp. 91 and 179), is inadequate to secure comprehension, and is not sufficiently illustrated either when first presented or later. In teaching, the first explanation of this subject has always to be a mere preliminary to that constant and various illustration and application which seem to constitute the only method of making it really clear. Without this—and every opportunity for this is strangely neglected by the author—that incorporation with the habits of thought of the student which alone can give him a command of modern chemistry has no chance of taking place. Surely a conception which, of all modern views, is by far the most fundamental to analysis, should have been driven home at every fair opportunity in a book intended for the student of analysis.

Even at the sacrifice of some of the elementary matter, space should have been found for the explanation in modern terms of such analytical methods and reactions as are usually omitted from text-books on general chemistry. Yet, so far as the reviewer can

discover, important topics like bead reactions, the solubility of magnesium hydroxide in ammonium chloride, the difference between double salts and salts of complex acids, the barium carbonate method, and the "solubility product" are not explained at all. The "normal solution" is defined (p. 112) as some physical chemists still unfortunately use the term (one mol per liter), and not as the analyst defines it. The behavior of the hydroxides of zinc (p. 389) and aluminum (p. 410) is ascribed to differing influences of acids and bases on the mode of ionization of the hydroxide, an assumption quite out of harmony with known facts. The precipitation of  $As_2S_5$  (p. 259) in concentrated hydrochloric acid is attributed to the interaction of hydrogen sulphide and arsenic acid, although  $AsCl_3$  is demonstrated to be the active substance by the result. Both of these cases might have furnished opportunities for beautiful applications of the theory of equilibrium. The paragraphs on indicators (p. 212) are misleading. The pink color of phenolphthalein in alkaline solution is not due to the ion of phenolphthalein itself, but to that of an isomeric colored acid.<sup>1</sup> Contrary to the statements in the book, this indicator is one of the best for weak acids, such as carbonic and phosphoric acids, provided they are not (like boric acid) weaker as acids than the isomer of phenolphthalein itself. The statement that this indicator cannot be used for titrating weak bases like ammonium hydroxide is correct, but the reason given is not. The cause of its lack of delicateness is the repression of the OH ions of the remaining hydroxide by the ammonium salts produced by the first stages of the titration.<sup>2</sup>

The book is worthy of a cordial reception, and it is to be hoped that a call for a second edition will speedily give opportunity for the needed modifications.

ALEXANDER SMITH.

INORGANIC CHEMISTRY SYLLABUS. BY HUBERT C. CAREL, B.S., Assistant Professor in the University of Minnesota. Third Edition. Minneapolis: H. W. Wilson, Publisher. 1902. 182 pp.

This book has been prepared for the students of the Freshman classes of the medical department of the University of Minnesota, and is a condensed compendium of the salient facts of descriptive inorganic chemistry. A few pages here and there are given to theoretical chemistry. The book suffers somewhat from errors,

<sup>1</sup> This Journal, 24, 568.

<sup>2</sup> *Am. Chem. J.*, 23, 406.



typographical and other, but contains an excellent index, which increases its value to medical students.

The problem of the best method of teaching chemistry in a medical school is as yet unsolved. A large proportion of men enter the school with little or no knowledge of chemistry, and are expected at the end of one year's study to find their way successfully through the intricate mazes of physiological chemistry. Alas for the teacher who is expected to perform this miracle!

J. L. H.

**KALENDER FÜR ELECTROCHEMIKER SOWIE TECHNISCHE CHEMIKER UND PHYSIKER.** VII Jahrgang, 1903. Mit einer Beilage. Edited by Dr. A. Newburger. xxxi + 583 + 448. Berlin: M. Krayn. Price, 4 marks.

In this valuable little book the editor has certainly succeeded admirably in his attempt to bring together material which is of value not only to the technical but also to the scientific worker. The separation of the technical from the theoretical branch has been more marked probably in electrochemistry than in any other subject and certainly the technical side has not gained by it. Through such works as this, we may look in the near future for a more intimate connection between the two branches of the subject which can not fail to be of great advantage to electrochemistry. There are but two criticisms to be made upon the make-up of the book, the lack of an index, and the binding of the Beilage as a separate volume, although its table of contents is given in the Kalendar.

J. LIVINGSTON R. MORGAN.

**BOTANY AND PHARMACOGNOSY.** BY HENRY KRAEMER, Professor of Botany and Pharmacognosy and Director of the Microscopical Laboratories in the Philadelphia College of Pharmacy. Published by the author. 384 pp.

The growing use of the compound microscope in the critical examination of powdered vegetable drugs has developed into a distinct branch of pharmaceutical study. It is perhaps needless to say that, in making a critical examination of vegetable powders, one must be familiar with the vegetable histological elements which make up the vegetable fabric, for no kind of pulverization will completely destroy the cell and obliterate its diagnostic features. The present volume, after dealing with plant morphology in Part I (100 pages), takes up the study of crude drugs, first giving their gross characteristics as found in their whole and dried condition. Following this is a scheme for the study of the

drug in the powdered state accomplished by the aid of the compound microscope and a few chemical reagents. It is in the latter part of the volume that we find the essentially new things, new to the English student. Important German and French works on powdered drugs have appeared, but in English, Prof. Kraemer's work is the second one in this country that has come from the press assuming the dignity of a text-book; hence it is to this *new feature* that especial attention should be directed. In this portion of the book we find an ingenuous key for the study of powders dividing them as follows: Powders of greenish color, powders of yellowish color, of brownish color, of reddish color, and of a whitish appearance. Each of these groups is subdivided in the following manner: I. *Crystals of Calcium Oxalate Present*.—(a) Calcium oxalate crystals, rosette shaped; (b) calcium oxalate crystals, monoclinic prisms; (c) calcium oxalate in crystal fibers; (d) calcium oxalate in cryptocrystalline crystals. II. *Calcium Oxalate Crystals Wanting*.—(a) Crystoliths of calcium carbonate present; (b) calcium carbonate crystals wanting, etc.

Then various sub-groups are made and subdivided very much as in botanical keys, making use of such characteristics as "Bast fibers present" or "Bast fibers wanting," "Stone cells present" or wanting and so on for other histological elements. This part of the work is perceptibly condensed, so much so that we fear it is of little use to the student unless he has constantly at his side the instructor who *knows* the book. What we have said of this portion of the volume is also applicable to other portions—it is extremely condensed and bears out fully what the author says in the preface: "It is written to meet the individual needs of the author in his work, as a treatise of botany and pharmacognosy and to supplement his lectures and laboratory demonstrations."

The illustrations in the work occupy the last portion of the volume very much as an appendix or afterthought. We are inclined to think that the placing of all the illustrations in the back of the book was poor economy. It would have been much better to have had these 13 pages interspersed in their proper places throughout the text. However, they are very good, and on excellent paper. The work is a valuable addition to the literature of pharmacy.

L. E. SAYRE.

**THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES.** BY DR. GEORG VON GEORGIEVICS, Professor at the Imperial and Royal State Trade School, Beilitz. Translated by CHAS. SALTER. London: Scott, Greenwood & Co. 1902. x + 306 pp. Price, \$4.50 net.

This is a concise text-book for students, which will not prove too abstruse for the general reader. The contents are almost entirely descriptive, and the material is, for the most part, well presented.

The book contains six chapters, *viz.*, The Textile Fibres; Washing, Bleaching, Carbonizing; Mordants and Mordanting; Dyeing; Printing; Dressing and Finishing. The chapter on dyeing is the most important section of the book. It opens with a discussion of the theory of color and color combinations; then follows an epitome of the author's views on the theory of dyeing. The mechanical theory is advocated, and a close analogy is traced between absorption of dye from the dye-bath by fibres, and solution of substances in two non-miscible liquids; the coefficient of the distribution of the dye is shown to be the same as the ratio of concentration, and it is argued that the dye-stuff "exists in different states of molecular constitution in the fibre and in the bath," the fibre absorbing simple molecules, leaving complex molecules in the bath. From this, various conclusions regarding the properties, fastness, etc., of dyes on fibres, are deduced.

The "solid solution" theory of Witt is rejected as not explaining the influence of the mechanical condition of the fibre on the "ratio of distribution," nor of the action of water on the dyed fibres. The chemical theory of dyeing is also rejected, after some discussion, with the sweeping assertion that "not one single fact is known that would indicate the probability of the occurrence of chemical combination between the dye-stuff and the fibre in dyeing."

The general excellence of the book is apparent, and but few defects may be noted. The discussion of Kellner's process for "electrolytic chlorine" might be clearer had a diagram of the apparatus been included. The directions for bleaching with sodium peroxide involve a procedure which would probably result in some loss of active oxygen. Errors in proof-reading occur on pages 2, 66, 67, 84 and 103; obscurity and some apparent carelessness of statement are shown on pages 24, 25 and 58, while in many places, the influence of the German syntax appears in the work of the translator.

There is a good index, but the omission of references to original articles is a serious defect.

F. H. THORP.

THE DYEING OF WOOLLEN FABRICS. BY FRANKLIN BEECH. London: Scott, Greenwood & Co. New York: D. Van Nostrand Co. 1902. viii + 223 pp. Price, \$3.50 net.

In the author's words the book is intended "to supply the dyer of woollen fabrics with a conveniently arranged handbook." Being designed for the use of practical dyers, it is liberally supplied with recipes applicable to special cases; these directions are frequently brief but sufficiently full to be understood by any one acquainted with the work of the dye-house. All reference to the composition and properties of the various dyes, mordants, etc., has been omitted as foreign to the purpose of the book. Chapter IV on the principles and practice of wool dyeing, the most important section of the book, contains a lucid account of the various methods of dyeing wools, though written somewhat after the cook-book style; the chapters on the dyeing of union fabrics, and of gloria, also contain much valuable information; the numerous recipes comprise, altogether, nearly 80 pages of the book. The teacher of textile coloring may also gain some useful hints from a perusal of these pages.

Typographic errors are few, but on page 4 we find *photoplasmic* and also an obscure sentence concerning the amount of curl in wool; on page 27 appears *covered* for *recovered*; the cut on page 55 is inverted.

The style is simple and clear and the absence of theoretical discussions will cause the book to find favor with many to whom such material has little attraction.

F. H. THORP.

PRINCIPLES OF DYEING. BY G. S. FRAPS, PH.D. New York: The Macmillan Co. 12mo. 270 pp. Price, \$1.60.

This little book sets out to give a systematic presentation of the principles underlying the art of dyeing, illustrated and emphasized by laboratory exercises. The plan of study is to take one or two typical members of each of five main classes of colors and study them with reference to their action toward the different fibers. The groups of textile fibers are next taken up and their physical and chemical characters and behavior under differing conditions noted. The operations of bleaching, scouring and dyeing are then explained in their main outlines. The groups of dye

colors are then discussed in somewhat fuller detail and the methods of dye-mixing and dye-testing described.

This plan has, in our opinion, been carried out with a notable measure of success and we believe the book would be well adapted to the use of students in dyeing classes as well as for dyers who wish to learn more of the theory underlying the art that they have learned in the dye-house. Prior to the appearance of this book, the best little book covering this ground was Hummel's "Dyeing of Textile Fabrics," but this book we believe to be the better of the two for the purpose it has in view. We can, therefore, recommend it quite cheerfully as worthy of an endorsement, and believe that it will find acceptance at the hands of those looking for a convenient manual on this subject.

S. P. SADTLER.

SEALING-WAXES, WAFERS, AND OTHER ADHESIVES. BY H. C. STANDAGE.  
London: Scott, Greenwood & Co. 1902. 95 pp. Price, \$2.50 net.

The first thing that strikes one in looking at this book is that two dollars and a half is a large sum to pay for a book of about 20,000 words, equal to about one-third of one of the monthly numbers of this Journal, made up, apparently, of recipes culled from the technical papers. Half of the book is devoted to sealing-waxes. There is a short but clear and intelligible description of this process, a brief account of materials used, and a large number of formulas, all of which are probably practical, and useful to the amateur. But the amateur is not likely to make a very fine article, and probably almost any formula is good enough for him, while the professional will always work out his own. Four pages are given to an interesting account of wafers. The rest of the book is on cements and pastes. The statement is made that "gelatine differs from glue in its chemical nature, but in physical characteristics is very similar"; also "this fact" (the insolubility of glue in oil) "has not been made full use of, as, for example, in the preparation of a glue compound that could be used as a paint for coating the inside or outside of barrels containing such volatile fluids as benzene, etc." I had supposed that every manufacturer in the world used glue to line the barrels for benzine, turpentine, oil, varnish, etc., and I still think so. "Flour, as a material for producing adhesives, depends on the gluten it contains." No doubt gluten is useful, but flour also contains starch, which has some repute as an adhesive, and starch is nowhere mentioned in the

book except once as a material from which dextrin is made and in one formula for a liquid glue, of which starch is to make one-tenth the total solids. The flour pastes and the glues are very good, but any one who expects to learn from this or any other book how to make such a paste, for example, as the "library" and "photographic" pastes now on the market, will be disappointed. Among the cements, I note the conspicuous absence of the old and reliable litharge and glycerin mixture, and all the asphaltum compounds. On the whole, it may be said that the book is very good, what there is of it, but as to its being the work of an expert there may be some doubt. A good book on glue alone, by a real expert, would be "mighty interesting reading" and it would be new.

A. H. SABIN.

**THE UTILIZATION OF WASTE PRODUCTS. A TREATISE ON THE RATIONAL UTILIZATION, RECOVERY AND TREATMENT OF WASTE PRODUCTS OF ALL KINDS.** BY THEODOR KOLLER. Translated from the German Second Revised Edition by a Technical Chemist. London: Scott, Greenwood & Co. New York: D. Van Nostrand Company. 8vo. viii + 279 pp. Price, \$3.50 net.

This book is in many respects opportune. Notwithstanding the fact that modern practice in manufacturing requires that everything which may find useful application shall be recovered and utilized, it is nevertheless true that many products are still allowed to waste while preventive methods are being eagerly sought. Experience in this country as well as abroad has shown that frequently utilization of waste, forced by legislative enactment by states and municipalities, has protected important industries from ruin, and that substances considered nuisances not only by producers but by their neighbors have become important sources of profit. We need only refer to the practice forced upon the meat-packing industries of this country to find apt illustration of this fact. The book before us calls attention to many of the wastes available and describes methods whereby they may be recovered. These descriptions are professedly for the greater part comparatively brief abstracts of papers published in various works and periodicals but few being the outcome of the experience of the author and many of them scarcely up to the standard of every-day practice. The source of information in each case is carefully given so that further details may readily be found, if desired. The book will prove useful in many hands and serve as a source

of suggestion and as a guide in the side lines of the various industries, particularly to those of limited practical experience.

WM. MCMURTRIE.

**THE UTILIZATION OF WOOD-WASTE.** BY ERNST HUBBARD. Translated from the German by M. J. SALTER. London: Scott, Greenwood & Co. 1902. 12mo. 192 pp. Price, \$2.50.

This little book is a translation of the second revised edition of one of the well-known Hartleben Library of technical manuals and deals with the various methods and proposed methods for utilizing sawdust and similar waste for the production of chemical products. It was one of three which have appeared in this library, the others being "Das Holz und Seine Distillations-producte," by Dr. George Thenius and "Die Verwerthung des Holzes auf chemischen Wege," by Dr. Jos. Bersch.

This work takes up first the employment of sawdust as fuel either with or without the simultaneous recovery of charcoal and the products of distillation. This is a very important subject and one to which practical chemists have given some considerable attention, as in lumber districts where sawmills abound a profitable utilization of the sawdust would be desirable. Many of the older forms of retorts for the continuous carbonization of sawdust by means of endless screws, etc., have, however, been given up in practice because of the difficulties caused by the moisture in the sawdust. This has been overcome in some cases by briquetting and previous drying of the briquettes or by the use of a preparatory drying chamber through which the moist sawdust passes on a sheet-metal conveyor or before it goes into the distillation chamber proper. The earlier briquetting procedure of Bergmann is described but we find no mention of the later, more successful, Heidenstam Swedish method.

The manufacture of oxalic acid from sawdust is very fully described and the means of purifying the product given.

The manufacture of ethyl alcohol and organic dyes from waste wood is also referred to but these proposed methods are as yet of little practical value.

The manufacture of artificial wood and plastic compositions for moldings is a much more important matter and is very satisfactorily described.

The employment of sawdust as an ingredient of blasting-powders and explosive mixtures is similarly very fairly dealt with.

The book is well printed and presents a neat and attractive appearance and will no doubt be found to be a source of much useful information.

S. P. SADTLER.

PAPERS ON ETHERIFICATION AND THE CONSTITUTION OF SALTS. BY ALEXANDER W. WILLIAMSON (1850-1856). Alembic Club Reprints, No. 16, Edinburgh. The Alembic Club, Chicago: The University of Chicago Press. 1902. Price, 40 cents.

The study of the original, classical papers, which have been of epoch-making significance in the development of chemistry, cannot be too earnestly commended. The Alembic Club of Edinburgh is performing a valuable service in making a series of these papers easily accessible. The papers are published in a neat cloth binding. Previous numbers of the series, as well as the one mentioned above, may be obtained from the University of Chicago Press.

W. A. N.

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#### INVESTIGATION OF THE PURITY OF CHEMICALS.

At the suggestion of Professor F. W. Clarke and others, a committee was appointed at the last meeting of the Society to investigate the purity of chemicals, especially reagents, as sold by dealers. It is a common experience that many articles marked "pure," "chemically-pure," or "C. P." are far from satisfactory, and it is believed by many analysts that the quality of reagent chemicals has grown worse instead of better in the last few years. At any rate the matter is of such importance as to merit investigation. The committee, which consists of Charles Baskerville, L. M. Dennis, W. F. Hillebrand, H. P. Talbot and the president of the Society as chairman *ex-officio*, is collecting data to show the extent of the evil of adulteration or wrong labeling, and requests information from all members of the Society who have had experience in the matter. This information should be sent to Professor H. P. Talbot, Massachusetts Institute of Technology, Boston.

The committee will be glad also to receive suggestions as to the best means of practically correcting the present unsatisfactory condition.



# THE JOURNAL

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## A NEW STABILITY TEST FOR NITROCELLULOSE POWDERS.

BY ALBERT P. SY.

Received March 30, 1903.

STABILITY tests, sometimes also called "heat tests," are applied to explosives to determine their stability or keeping qualities. During the process of manufacture these tests are made to determine if the product has been sufficiently purified, *i. e.*, freed from substances which might cause it to decompose spontaneously.

Before describing the new test, the more important and most used of the old tests, including the four used by the Ordnance Department, U. S. Army, are briefly mentioned; this is done so as to point out the weak points of these tests to those not familiar with them.

### THE POTASSIUM-IODIDE-STARCH, OR ABEL TEST.

This test is prescribed and made by the Ordnance Department, U. S. A., as follows: 1.3 grains of the sample (air-dried) is placed in a test-tube in which there is suspended a test paper of potassium-iodide-starch, moistened to one-half its length with a 50 per cent. glycerin solution. This tube is then immersed in a bath kept at  $65.5^{\circ}\text{C.} \pm 1^{\circ}$ , for nitrocellulose, and at  $100^{\circ}\text{C.} \pm 1^{\circ}$ , for nitrocellulose powders. The test is ended at the appearance of a brown

or blue line on the test paper. For a good nitrocellulose this discoloration must not take place in less than forty minutes (at  $65.5^{\circ}$ ), and for a good nitrocellulose powder in not less than ten minutes (at  $100^{\circ}$ ). Powders containing nitroglycerin should stand this test for twenty minutes at  $65.5^{\circ}$ .

The discoloration of the test paper is due to the action of free iodine on the starch, the iodine being liberated from the potassium iodide by impurities or products of decomposition, principally oxides and acids of nitrogen volatilized from the explosive. This test is of some value to the manufacturer to determine whether his product has been thoroughly purified, and the test could be called "purity test" more appropriately than a stability test. When applied to finished products, this test has many weak points, as follows:

(1) It shows, in cases of decomposition of the sample during the test, only the beginning and not the continuation of the decomposition; it is more important to know how decomposition proceeds than when it begins.

(2) Traces of unstable nitro-compounds would show a nitrocellulose or powder in which they are found by this test to be bad; yet these traces of unstable compounds might not cause a decomposition of the explosive, if stored under ordinary conditions, and, considering that there is no indication of the effect of these unstable compounds, this test does not indicate the keeping qualities of the explosive.

(3) Traces of solvents left in a powder affect this test.

(4) The weakest point of this test is the fact that it can be masked by a number of substances which are sometimes added to the explosive for this purpose. These substances are mercuric chloride, mercury salts, carbonates, alkalies, amines, acetic ether, acetone, oils, vaseline, aniline, etc. Explosives containing masking substances are not accepted by the Ordnance Department.

(5) The test is affected by the condition of the sample, size of grains, whether freshly prepared for testing or exposed to air, and by moisture content. Charges of static electricity, which a powder acquires on rasping or cutting, affect the results of this test. Experiments along this line are being made by Capt. H. C. Aspinwall.

(6) Slight differences in test papers greatly affect the results of this test. (The test papers used by the Ordnance Department

are made in large quantities by Eimer and Amend, of New York, according to specification, thereby insuring greater uniformity than if made at different laboratories in small quantities. Manufacturers who have contracts with the government are supplied with these papers.)

(7) The personal equation of the operator enters as a factor in causing variations. It is no easy matter to decide just when there is the first appearance of a brown line on the test paper.

On account of the points mentioned, duplicates of the same powder have been known to vary from twenty to thirty minutes. The potassium-iodide-starch test has long been known to be unreliable, and the Ordnance Department condemns no explosives on results of this test alone.

#### THE ZINC-IODIDE-STARCH TEST.

This is a modification of the test just described, zinc iodide being used instead of potassium iodide (temperature 80° C.). Zinc iodide is more sensitive than potassium iodide, and also acts as a preservative of the test-paper. However, a greater sensitiveness is in no way an improvement of the potassium-iodide-starch test, and results obtained at this laboratory show that this test is not more reliable than the original, having all the weak points of the latter.

#### THE GUTTMANN TEST.

Instead of using a potassium-iodide-starch paper, Guttman recommended<sup>1</sup> a test paper moistened with a solution of diphenylamine in sulphuric acid. He claimed for his test the following advantages: (1) Not as sensitive as the potassium-iodide-starch test; (2) test papers more easily prepared; (3) masking substances do not interfere. The temperature used is 70° C., and nitrous fumes turn the colorless paper to a greenish-yellow and finally blue.

Thomas says<sup>2</sup> the diphenylamine test is unsatisfactory; it may be masked by the addition of diphenylamine to the explosive to be tested. Guttman himself admits that the blue color sometimes fails to appear. Moisture in the sample affects the test. Thomas as well as others failed to get a sharp end-reaction. The Guttman test was tried at this laboratory but gave unsatisfactory results, and was discontinued. Aspinwall,<sup>3</sup> Spica,<sup>4</sup> and Thomas

<sup>1</sup> *Ztschr. angew. Chem.* (1897), p. 233; *J. Soc. Chem. Ind.* (1897), p. 283.

<sup>2</sup> *Ibid.*, (1898), p. 1027.

<sup>3</sup> *J. Soc. Chem. Ind.*, May 31, 1902.

<sup>4</sup> *Rivista*, August, 1899.

found sufficient objections, after trial, to discard it. Major Nathan says<sup>1</sup> the test fails when testing volatile explosives, such as nitroglycerin, the latter being decomposed by the sulphuric acid on the test paper.

#### THE HESS TEST.<sup>2</sup>

Nitrocellulose is heated to 70° C. in a tube and, by means of a current of air, the volatile products of decomposition are carried into a dilute potassium-iodide-starch solution. Five observations are made: four colorimetric readings on the potassium-iodide-starch solution, and the time required for explosion of the sample. This test shows the beginning, and roughly, and for a short time also, how decomposition proceeds. The potassium-iodide-starch solution, however, is far too sensitive, and may show decomposition which in reality does not indicate instability of the explosive. Masking substances interfere as mentioned under the potassium-iodide-starch test, and results are affected by solvents in the sample, condition of the sample, difference in the testing solution, and personal equation of the operator.

#### THE HOITSEMA TEST.<sup>3</sup>

The explosive is heated for fifteen minutes at a constant temperature, and then, by means of a current of carbon dioxide, the volatile products of decomposition are passed through glass wool moistened with Guttman's diphenylamine solution. This operation is repeated, lowering the temperature 10° each time until a temperature is found at which no products of decomposition are found which give a color reaction with the test solution, this being considered the point at which decomposition ceases.

The test is too sensitive and subject to most of the objections mentioned under previous tests, especially under the Guttman test.

#### THE EXPLOSION TEST.

A small sample of the explosive (usually 0.1 gram) is placed in a strong test-tube which is then tightly corked and placed in a paraffin bath at 100° C. The bath is now stirred and heated so that the temperature increases 5° per minute. The temperature is noted at which the sample explodes.

<sup>1</sup> *J. Soc. Chem. Ind.* (1901), p. 10.

<sup>2</sup> *Mitth. u. Gegenst. d. Artill. u. Geniewesens* (1879), p. 345; *Dingler's poly. J.*, 234, 43.

<sup>3</sup> *Ztschr. angew. Chem.* (1889), p. 705.

A good nitrocellulose should not explode under 186° C.

A good nitrocellulose powder should not explode under 177° C.

A good nitroglycerin powder should not explode under 170° C.

These explosion points are required by the Ordnance Department; those required by other governments differ considerably. Judging from a great number of explosion tests made at this laboratory it seems that this test is reliable when the explosive is either very good or very bad. Variations in results may be caused by difference in manipulation of the test, especially in raising the temperature; the following table shows the effect on the explosion point of raising the temperature 1°, 2.5°, and 5° per minute, on powders Nos. 175, 178, 179 and 180.

Powder.	1°.	2.5°.	5°.
175	164	174.5	177
178	170	176	178
179	173	176	177
180	167	174.5	179

This table also shows that greater differences between the explosion points are obtained when the temperature is raised only 1° instead of 5° per minute.

#### THE THOMAS TEST.<sup>1</sup>

In this test the sample is heated in a glass-stoppered tube in an oil-bath for eight hours daily. A good nitroglycerin powder should stand four days' heating at 94°-96° C. without developing brown fumes ( $N_2O_4$ ); a good nitrocellulose and nitrocellulose powder should not show fumes before three days, using a temperature of 99°-101° C.

These temperatures are too low to produce a decisive decomposition which may be observed by the appearance of brown fumes; it is hard to say just when brown fumes appear. Varying amounts of moisture and solvents in the powder will give different pressures in the closed tube, and consequently different results, since pressure affects decomposition.

#### THE 135° C. TEST.

Two and one-half grams of the explosive, and a piece of blue litmus paper are placed in a strong test-tube (320x18 mm.); the latter is tightly corked and placed in a bath at 135° C. Three observations are made: (1) Reddening of the litmus paper, (2)

<sup>1</sup> *Ztschr. angew. Chem.*, p. 1027 (1898).

brown fumes ( $N_2O_4$ ), and (3) explosion of the sample. The minimum time as required by government specifications for these three observations is as follows:

	Litmus red.	$N_2O_4$ .	Explosion.
Nitrocellulose.....	30 min.	45 min.	5 hrs.
Nitrocellulose powder .....	1 hr., 15 min.	2 hrs.	5 hrs.
Nitroglycerin powder .....	30 min.	45 min.	5 hrs.

After subjecting a large number of samples to this test it has been found that any one of these three observations alone is not always a correct indication of the condition or stability of the sample.

To illustrate:

	Litmus red.	$N_2O_4$ .	Explosion.
Powder No. 445.....	1.30	3.30	None in 5 hrs.
Powder No. 265.....	2.05	2.45	3.25

Powder No. 445 is a good, stable powder, while No. 265 is unstable; yet the former reddened litmus paper before the latter. Again:

	Litmus red.	$N_2O_4$ .	Explosion.
Powder No. 265.....	2.05	2.45	3.25
Powder No. 610.....	2.05	2.45	None in 5 hrs.

Here the first and second observations are alike, but No. 610 did not explode and was shown by other tests to be a perfectly stable powder. No. 265 is bad. These examples show that the reddening of blue litmus paper and the appearance of brown fumes in this test, as well as in all other tests where these observations are made, are not always reliable indications of the relative stability of powders. The temperature of  $135^\circ$  C. is usually considered too high for stability testing as it may cause decompositions not always dependent upon the stability. In this test it is sometimes difficult to decide when the litmus paper is red, and when there is the appearance of brown fumes; two operators may vary thirty minutes or even more in the observations of this test. Different makes of litmus paper give different results; the papers used by the Ordnance Department are made according to specifications by Eimer and Amend, and of as nearly uniform quality and sensitiveness as possible.

By keeping all conditions as nearly uniform as possible, this test becomes one of the best of its kind.

#### THE VIEILLE TEST.

Ten grams of the explosive are placed in a strong glass tube or bottle, a piece of blue litmus paper is placed above the sample and

the tube closed air-tight; the tube is then heated in an air-bath at  $110^{\circ}$  C. until the litmus paper is completely reddened. The time required for this reddening is noted, the bottle removed and opened; this operation is repeated daily until the time required to redden the litmus paper is one hour or less; of course a clean bottle and fresh paper is used each day. The daily times are added and the total (or accumulated) time should not be less than thirty hours for large powders (for 5-inch gun or larger), twenty hours for small powders (less than 5 inches), and ten hours for nitrocellulose. On account of the volatility and danger of explosion of nitroglycerin, powders containing it cannot be tested by this method.

The reddening of the litmus paper indicates only acid products of decomposition and is affected by the moisture-content of the sample. It is practically impossible to have all the Vieille bottles equally tightly closed; experiments have shown that pressure is an important factor in the decomposition of nitrocellulose. The personal equation of the operator affects the readings; varying results are obtained unless the litmus papers used are uniform. The papers used by the Ordnance Department are the same as described under the " $135^{\circ}$  test."

Results obtained by the Vieille test are reliable only when the explosive is very good or very bad.

#### THE WILL TEST.<sup>1</sup>

Nitrocellulose is decomposed at  $135^{\circ}$  C. and by means of a current of carbon dioxide, the products of decomposition are carried into a reduction tube containing a heated spiral of copper gauze; this reduces the nitrogen compounds to nitrogen gas which is measured over sodium hydroxide. The nitrogen is measured at regular intervals, and the rate of evolution is taken as an index of the decomposition. A nitrocellulose, which by this test gives equal quantities of nitrogen in equal intervals of time, is considered by Will to be in "the limit state of purification," and therefore as stable as possible. Considering the principle of this test, and in theory it should give better results than any of the other tests so far described.

Will's test was thoroughly tried by Mr. C. P. Beistle of this laboratory, no expense nor time being spared in setting up the

<sup>1</sup> *Mitth. a. d. Centralstelle f. Wissenschaft. Untersuch.*, December, 1900; *Neu Babelsberg*; also *abst. J. Soc. Chem. Ind.*, June 30, 1900.

rather elaborate and complicated apparatus required, and in conducting the test. The results obtained were unsatisfactory and the test was abandoned.

The following reasons are given as the cause of unsatisfactory results:

(1) The temperature  $135^{\circ}$  C. is too high for stability testing purposes.

(2) The decomposition is measured only by the nitrogen evolved.

(3) From Professor Will's experiments and diagrams it is not at all clear where to draw the line between a stable and an unstable product.

(4) The statement is made in Professor Will's report that for a certain nitrocellulose, heated for thirty hours and losing one-fourth its original nitrogen, the evolution of nitrogen in equal intervals of time was identical, while in another place it is stated that 10 grams of nitrocellulose gave four times the amount of nitrogen that was given off by 2.5 grams. This latter statement is correct, judging from our own experiments, but it contradicts the former, since the amount of unchanged nitrocellulose in the former experiment is constantly decreasing.

(5) It is practically impossible to buy or make carbon dioxide which is free from air; and as it is difficult to pass carbon dioxide through the apparatus at a uniform rate, the air-content of the gas gives rise to serious errors, and if the current be too fast it may cool the sample, and it will not be completely absorbed by the sodium hydroxide solution; if too slow, the gases of decomposition are not carried away fast enough, which may effect the decomposition, as stated by Professor Will.

(6) If the reduction tube and copper spirals are not heated sufficiently high, or the current of carbon dioxide is passed too fast, some of the products of decomposition may escape reduction.

(7) Unstable products are liable to explode, which might cause considerable annoyance both to the operator and the apparatus.

#### THE NEW TEST.

From a study of the old stability tests, and considering what such tests really ought to show, it must be apparent that none of those in use now are entirely satisfactory. At this laboratory,

NOTE.—For a more detailed description of these tests and illustrations of apparatus, see article by the writer in *Journal of the Franklin Institute*, March, 1903.



explosives are subjected to the potassium-iodide-starch test, explosion, 135° C., and Vieille tests; having made these tests on each sample received, it is unlikely that a really unstable or dangerous explosive has ever been or ever will be accepted. But contradictory results are often obtained (see Table I), due to weak points of these tests.

During a series of experiments for Captain B. W. Dunn, Ordnance Department, U. S. Army, to examine the behavior of powders when subjected to higher temperatures it was noticed that for the same temperature there is a great variation in the behavior of different powders. (Credit is due to Captain Dunn for suggestions and aid in this work.)

If the decomposition of powders increases as the temperature increases, then the behavior of these powders at higher temperatures is an index of their behavior at low temperatures. To prove the relation between temperature and decomposition, a number of powders were heated on watch-glasses in air-baths regulated to different temperatures; at regular intervals the samples were cooled in a desiccator, weighed, and the percentage of loss, due to decomposition and volatilization, calculated. In this series of experiments, powder No. 179, a good nitrocellulose powder, was subjected to temperatures<sup>1</sup> of 80°, 100°, 110°, 115° and 135°; the losses at these temperatures are shown in Fig. 1. After the loss of moisture and solvents, the volatilization of the powder proceeds relatively slowly, but with an increasing rate until a condition is reached which corresponds to the breaking-point of the powder, the action being similar in many respects to that of a metal test specimen in passing its elastic limit. The new test promises to give us, then, *The Elastic Limit of Powder Resistance to Heat*, and this is the new measure proposed for the powder's stability. In Fig. 1, the 110° and 115° curves locate this elastic limit more definitely than the others, the 110° curve at 12, and the 115° curve at 8 days. It is also located at 12 days by the 100° curve, but this temperature is evidently too low. It was not located in thirty days by a temperature of 80°. At 135° no initial stage of resistance could be detected, and it is assumed that at this temperature all powders begin to break down immediately. From the curves on Fig. 1, it is apparent that the best temperature for determining the elastic limit of a normal powder is about

<sup>1</sup> All temperatures are °C.

TABLE I.

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test.			135° C. test.			New 115° C. test.			
		Orig- inal. Min.	One year later. Min.	Ex- plosion. Test C.	Litmus red.	N <sub>2</sub> O <sub>4</sub> .	Explosion limited to 5 hours.	Viette test. Hr., min.	Daily loss exceeded 1 per cent. 7th day From beginning	Maximum daily loss. 12th day	Total loss for 6 days. Per cent.
4-11	0.25 × 0.5	15	15	174	1 : 40	None	None	....	9	8	6.52
4-25	0.56 × 0.7	39	30	171	1 : 52	None	None	....	Not reached	8	10.22
155	0.62 × 1.0	16	13	...	2 : 00	None	None	27 : 20	9	Not reached	4.72
179	0.25 × 0.6	35	23	177	4 : 00	None	None	27 : 05	9	13	5.34
197	0.25 × 1.0	..	12	176	1 : 55	None	None	19 : 40	9	Not reached	4.73
210	0.7 × 1.7	28	11	177	2 : 50	None	None	49 : 40	12	14	7.16
262	0.45 × 1.12	18	12	172	3 : 00	None	None	49 : 15	Not reached	Not reached	7.45
265	0.8 × 1.8	15	10	171	2 : 05	2 : 45	3 : 25 3 : 55	29 : 05	From beginning	8	12.54
293	0.8 × 1.8	15	11	166	1 : 20	2 : 20	None	33 : 30	From beginning	7	15.89
294	0.7 × 1.7	10	7	177	2 : 15	None	None	46 : 25	14	Not reached	6.88
326	0.45 × 1.5	30+	30+	161	: 50	2 : 47	3 : 00 4 : 00	24 : 40	From beginning	6	19.70
344	0.7 × 2.0	13	13	150	1 : 15	2 : 22	3 : 00 4 : 15	25 : 10	From beginning	5	19.39
373	0.75 × 1.6	30+	5	175	2 : 35	None	None	36 : 50	13	16	6.44
387	0.4 × 0.9	9	30+	174	3 : 20	None	None	22 : 50	11	Not reached	5.11
389	0.4 × 0.75	10	..	178	1 : 00	None	None	12 : 40	Not reached	Not reached	5.49

TABLE I.—(Continued).

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test.			135° C. test.			New 115° C. test.			
		Orig. sal. Min.	One year later. Min.	Explosion. Test C.	Litmus. red.	N <sub>2</sub> O <sub>4</sub> .	Explosion limited to 5 hours.	Viette test. Hr., min.	Daily loss, per cent.	Maximum daily loss.	Total loss for 6 days. Per cent.
391	0.25 × 0.36	12	18	168	: 50	1 : 45	2 : 45 2 : 50	8 : 35	From beginning	5	21.55
396	0.65 × 1.7	20	12	173	3 : 20	None	None	21 : 45	14	Not reached	8.53
405	0.75 × 1.6	30+	17	175	2 : 00	None	None	19 : 15	From beginning	6	18.14
406	0.36 × 1.0	30+	30+	168	1 : 15	3 : 40	3 : 55	15 : 45	From beginning	6	18.80
407	0.6 × 1.3	30+	30+	167	1 : 50	2 : 25	2 : 35	15 : 50	From beginning	7	12.00
445	0.42 × 0.9	15	30+	176	1 : 30	3 : 30	None	31 : 40	11	17	4.83
544	0.25 × 0.63	21	14	176	2 : 15	None	None	30 : 20	Not reached	Not reached	5.11
546 F.A.	0.45 × 1.5	12	30+	170	1 : 20	None	3 : 00 3 : 40	6 : 50	From beginning	3	25.64
577	0.34 × 1.0	12	..	175	1 : 10	1 : 45	None	21 : 45	9	Not reached	6.74
608	0.12 × 1.0	30	..	175	1 : 10	4 : 30	None	16 : 05	6	10	6.05
610	0.8 × 1.8	16	10	178	2 : 05	2 : 45	None	30 : 35	14	Not reached	6.58
619	0.4 × 0.9	6	..	176	2 : 10	3 : 50	None	31 : 15	12	17	5.44
716	0.4 × 0.6	10	..	175	1 : 25	None	None	22 : 00	Not reached	Not reached	4.53
717	0.4 × 0.6	10	..	172	1 : 00	None	None	18 : 55	Not reached	Not reached	5.23

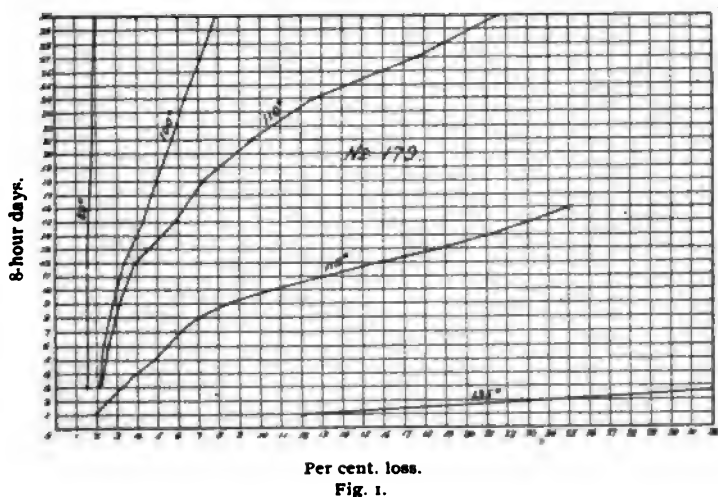
TABLE I.—(Continued).

Laboratory No. of powder.	Size of grain (inch).	Potassium iodide starch test.		155° C. test.			New 115° C. test.				
		Orig. Min.	One year later. Min.	Ex- posu- tion. Test C.	Litmus red.	N <sub>2</sub> O <sub>4</sub> .	Explosion limited to 5 hours.	Vetile test Hr., min.	Daily loss exceeded 1 per cent.	Maximum daily loss.	Total loss for 6 days. Per cent.
797	0.4 X 0.75	55	..	175	2 : 15	None	None	25 : 40	Not reached	Not reached	5.69
798	0.4 X 0.75	45	..	179	2 : 15	None	None	24 : 50	12	Not reached	4.77
799	0.4 X 0.75	60+	..	177	2 : 30	None	None	22 : 30	10	Not reached	4.32
800	0.62 X 1.0	30+	..	178	2 : 05	None	None	31 : 25	Not reached	Not reached	4.85
803	0.8 X 1.8	27	..	173	1 : 50	3 : 25 3 : 30	3 : 20	24 : 15	From beginning	9	12.37
834	0.4 X 0.87	30+	..	171	3 : 10	None	None	19 : 50	11	Not reached	5.90
836	0.48 X 0.95	30+	..	175	3 : 30	None	None	30 : 45	13	Not reached	7.07
922	0.75 X 1.12	15	..	177	2 : 00	None	2 : 45	31 : 00	Not reached	Not reached	5.00
924	1.0 X 1.75	10	..	175	1 : 40	None	2 : 45	31 : 10	Not reached	Not reached	5.50
926	1.12 X 2.0	10	..	179	2 : 05	None	3 : 25	31 : 00	Not reached	Not reached	5.99

115°. Fig. 2 shows 100°, 110° and 115° curves for a bad powder, No. 391. The elastic limit at 110° is located at nine days, and at 115° at three days. These results (shown in Figs. 1 and 2) prove that there is a definite relation between decomposition and temperature. They show also that a bad powder (No. 391) decomposes much faster, reaching the elastic limit sooner than a good one (No. 179) at the same temperature; after forty-eight hours' heating at 115°, No. 391 lost 21.55 per cent., while No. 179 lost only 5.34 per cent.

The relation between temperature and decomposition, and the fact that a bad powder decomposes faster than a good one having been proved by these results, it remained to be decided which temperature is best suited to distinguish a bad from a good powder. This required a long series of experiments. It is obvious, of course, that the lower the temperature used, the more nearly does the test approach conditions to which a powder is liable to be subjected during storage and handling; but, the higher the temperature used, the shorter will be the time required to show sufficient decomposition to distinguish between a good and bad powder. Although it is very desirable to shorten the time required for making a test, it is not advisable to sacrifice accuracy on this account.

As may be seen from Fig. 1, the decomposition of a powder at 80° is exceedingly slow; even at 100° it is still very slow (Figs.



Per cent. loss.  
Fig. 1.

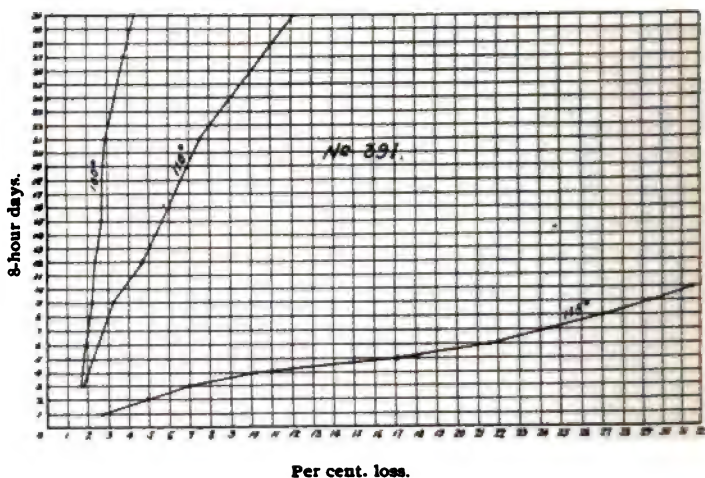


Fig. 2.

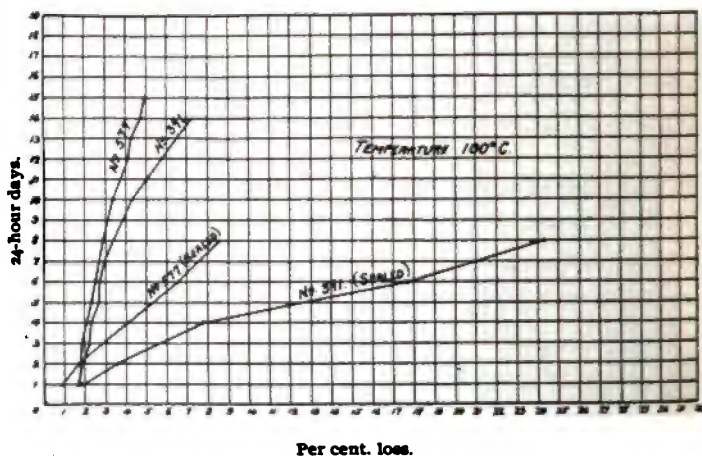


Fig. 3.

1, 2 and 3), but the difference between a good and bad powder becomes quite noticeable at  $100^{\circ}$ , as shown in Fig. 3 by No. 577 (good) and No. 391 (bad). However, the difference is not sufficient, and the time required is too long to be used as a practicable test. Decomposition is greatly increased at  $110^{\circ}$ , and the difference between good and bad powders becomes greater; this is shown in Fig. 4, where Nos. 619, 445 and 577 are very good, and Nos. 391, 326 and 546 F. A. are very bad powders, the others

shown being intermediate. Here again the time required to show the differences is still quite long, too long for practical testing.

The temperature was next increased to  $115^{\circ}$ , and, in order to avoid possible danger from explosions, the exposures were made for eight hours only (during working hours); at the lower temperatures the tests were allowed to run during the night. Three grades of powders were used for all tests—good, bad, and intermediate or doubtful. At  $115^{\circ}$ , decomposition takes place rapidly, and the difference between good and bad powders becomes apparent in a few days as shown in Figs. 5, 6 and 7, which will be more fully discussed later.

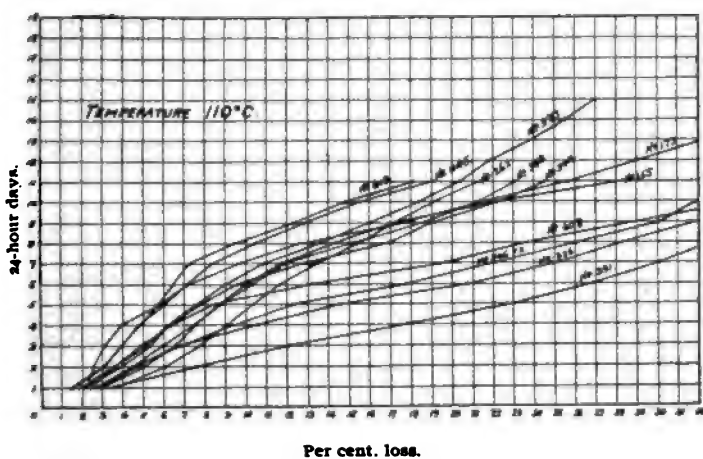


Fig. 4.

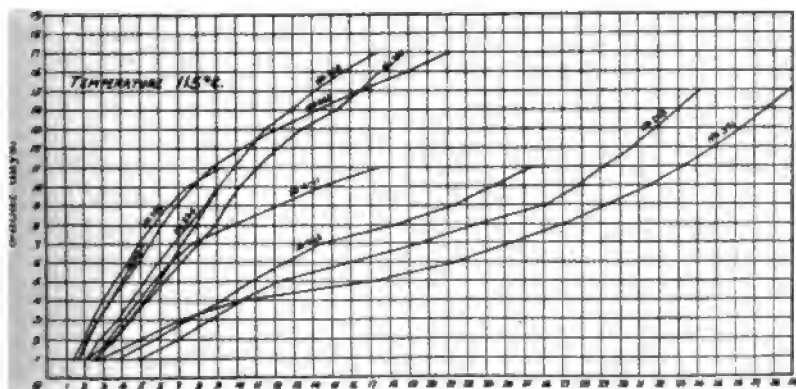


Fig. 5.

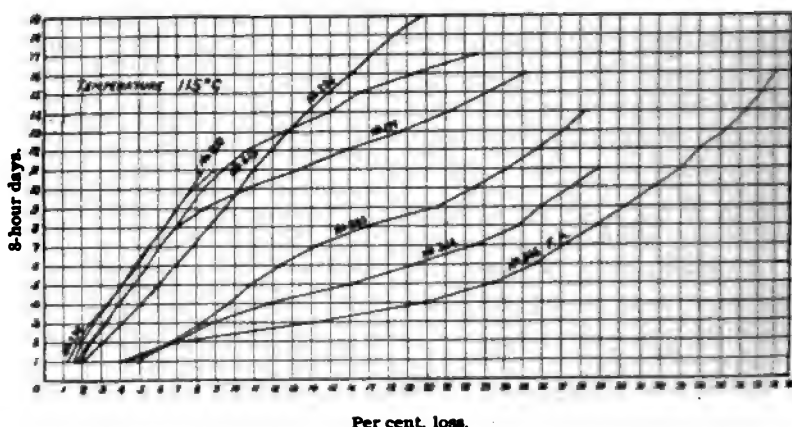


Fig. 6.

Some experiments were made at  $120^{\circ}$ ; the rate of decomposition increased at this temperature, but the difference between a good and bad powder did not seem as great as at  $115^{\circ}$ , all powders decomposing more or less rapidly at  $120^{\circ}$ .

Experiments were made to determine the combined effect of heat and pressure on powders; the weighed samples were placed in small tin boxes and the latter sealed (soldered) air-tight; they were then exposed to  $80^{\circ}$  and  $100^{\circ}$ , the boxes opened and weighed at regular intervals. At  $80^{\circ}$  decomposition is slow, but more rapid than if the powder were heated in the open on a watch-glass, *e. g.*, No. 179 heated at  $80^{\circ}$  lost 9.90 per cent. in forty-one days when sealed, but lost only 2.85 per cent. when heated on a watch-glass at the same temperature and for the same length of time. For a reasonably short time of exposure the difference between a good and a bad powder at  $80^{\circ}$ , sealed, is small. At  $100^{\circ}$ , sealed, the difference between a good and bad powder becomes quite marked, as may be seen from Fig. 3; this figure also shows that the difference between a good (No. 577) and a bad powder (No. 391) is greater when sealed and decomposed under pressure than when heated in the open; the time required is also reasonably short. It will be observed that the effect of pressure is the same as that of an increase in temperature. It is probable that more extensive experience may result in the adoption of a "sealed" method of testing. A form of holder must be devised, however, better than the bottles used in the Vieille test. The sealing features of this holder must be reliable and convenient. It will



probably be of metal with a convenient method of sealing by pressure derived from a screw thread, and not depending upon a rubber gasket. In addition to shortening the time required for tests at a given temperature, the sealing method is preferred because it corresponds more nearly to the conditions of storage of powders. In fixed ammunition the powder charges are almost if not quite hermetically sealed to make the ammunition water-proof, and when stored in large metal-lined boxes in magazines the quantity of powder is very large as compared with test specimens, and the space for the volatile matter to collect very small. It is intended to hermetically seal the storage cases by soldering.

From these preliminary experiments it appeared that when heating the powders unconfined,  $115^{\circ}$  gave the best results. Considering the importance of a knowledge of the stability of a powder, the time required to get results at  $115^{\circ}$  may be considered reasonably short.

For some of the preliminary tests an ordinary sheet-copper

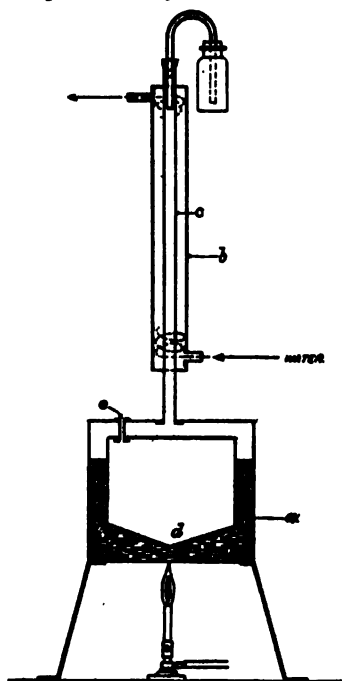


Fig. 7.

air-bath or oven was used; the temperature was regulated

by means of a gas regulator or thermostat; however, it was a matter of considerable difficulty to keep the oven at  $115^{\circ}$ , and under the most favorable conditions it was impossible to avoid variations of  $+1^{\circ}$  or  $2^{\circ}$ . In order to obtain a more uniform temperature, an oven shown in Fig. 1 (diagrammatic sketch) was devised. The oven part is double-walled, of heavy sheet-copper, similar to the ordinary double-walled water-ovens; but in order to prevent bumping and jarring, which is a common fault of all water-ovens, the bottom part of the inner wall was made slightly V-shaped; this arrangement causes the contents of the oven to boil quietly, and effectively prevents bumping. A reflux condenser in the top of the oven prevents the volatilization of the boiling mixture. The latter consists of commercial xylene and toluene in such proportion that when the mixture is boiling, the temperature of the air on the inside of the oven is  $115^{\circ}$ . This arrangement is simple and has been found perfectly satisfactory, the temperature varying less than  $0.5^{\circ} +$  or  $-$ . The opening *E* is for a thermometer; the oven has two shelves, and an opening (closed by a screw plug) for introducing the xylene-toluene mixture; these are not shown in the sketch.

The test adopted, pending further developments, is as follows: From one to four whole pieces of the powder to be tested are weighed on a watch-glass and heated for eight hours in the  $115^{\circ}$  oven; the sample is allowed to cool in a desiccator and weighed; the loss in weight is calculated to percentage. This is repeated from day to day until completion of test (6 days, or less).

A large number of powders have been subjected to this method of testing, and some of the results are shown in Figs. 5, 6 and 7. In Fig. 5 the powders numbered 391, 293 and 265 are bad, 4-11 are doubtful, while the others are good. In Fig. 6, Nos. 546 F. A., 344 and 803 are bad, the others are good. In Fig. 7, Nos. 326, 406 and 405 are bad, 4-25 are doubtful, while the others are good. The powders indicated as bad had previously been diagnosed as such by a careful study of the combined results of four of the old stability tests (see Table I).

In the new test at  $115^{\circ}$  during the first day's heating, a good powder loses approximately its moisture and volatile matters; after this, the daily loss is less than 1 per cent., but gradually increases until a maximum is reached, after which it slowly decreases. The daily loss of a good powder does not exceed 1 per

cent. before the sixth day, often not before the tenth day. The maximum daily loss is usually not reached before the eighth day. A bad powder usually loses more than its moisture and volatile matters on the first day; the daily loss is more than 1 per cent. before the sixth day and the maximum daily loss occurs before the eighth day.

*The total loss of a good powder for six days is less than 10 per cent.; bad powders lose considerably more than 10 per cent. in six days.* By this test, therefore, it is possible to obtain reliable indications as to the stability of a powder in six days of eight hours each. In special cases where it is necessary to get results more quickly, the exposures could be made for twenty-four hours, or weighings could be made at eight-hour intervals, and results obtained in a little over two days.

After prolonged heating, good and bad powders approach the same total loss (Fig. 8). Preliminary analyses of the residues

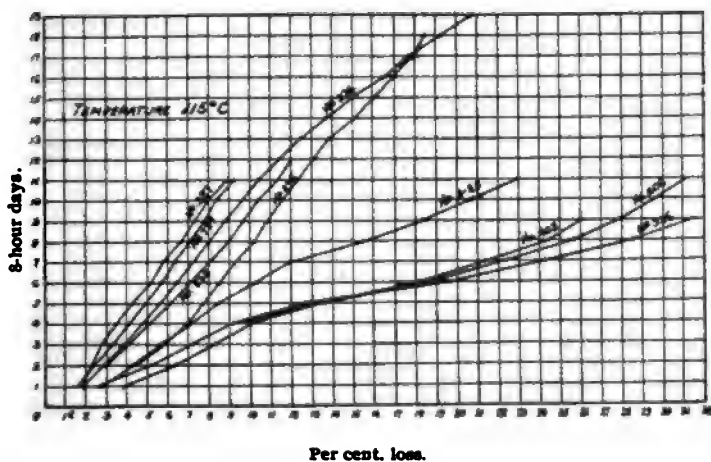


Fig. 8.

from these heat tests indicate that the decomposition of the powders by heat is a complex reaction or process. Most powders become quite brittle and porous but still retain their shape, the decomposition being a sort of destructive distillation; a few powders, usually bad, lost their shape, being fused and soft while hot, porous and brittle when cold. The percentage of nitrogen decreases as the total loss increases. With a total loss of 55 to 56 per cent. the nitrogen in the residue was found to be 4.31 to

4.91 per cent. (15 samples examined; original nitrogen 12.37 to 12.60 per cent.). This agrees with the fact that the loss curves

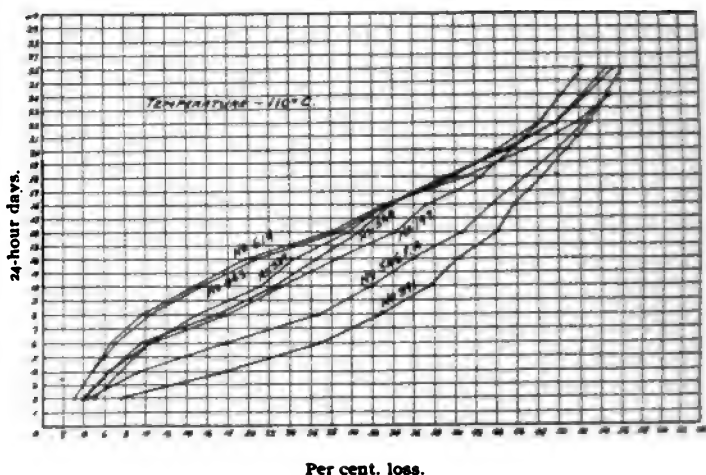


Fig. 9.

(Fig. 8) are close together at 55 to 56 per cent. "Acetone insoluble" nitrocellulose increases with total loss:

Total loss. Per cent.	"Acetone insoluble" nitrocellulose. Per cent.
41.37	0.12
55.67	0.72
65.08	6.99

Analysis of residues as well as volatile products of decomposition

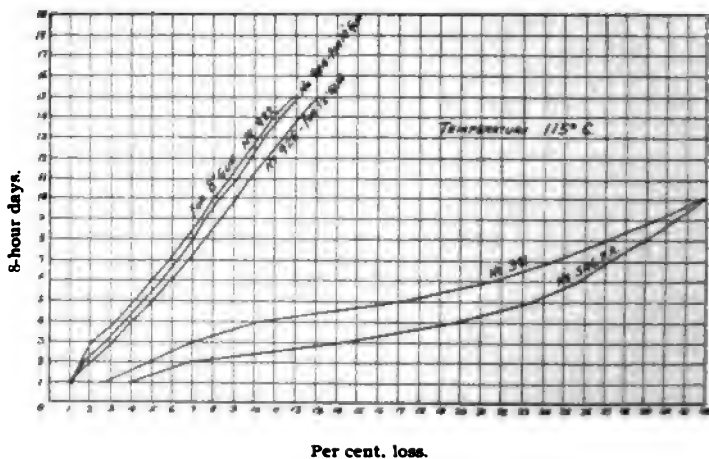


Fig. 10.

is to be the subject of future investigation. The size of the grain of powder affects the decomposition slightly, but not sufficiently to be taken into consideration when distinguishing a bad from a good powder by this test; decomposition of a powder increases slowly as the size of the grain increases; this is shown in Fig. 9. Powders Nos 922, 924 and 926 are made from the same lot of nitrocellulose, as nearly alike as possible, except in size as indicated in Fig. 9. Powders Nos. 391 and 546 F. A. are bad powders, shown for comparison.

Results of four old stability tests, and of the new test, are shown in Table I. A study of this table shows that the old tests often give contradictory results, due to weak points of these tests as pointed out in their description. The requirements for a good or stable powder by the old tests are, for

Potassium-iodide-starch test, 10 minutes.

Explosion test, 177° C.

135° test { Litmus red, 1.15.  
N<sub>2</sub>O<sub>4</sub> fumes, 2.00.  
Explosion, none in five hours.

Vieille test { Twenty hours for five-inch powders.  
Thirty hours for powders larger than five-inch gun.

Table II, made from Table I and the above requirements, shows how results from the old tests often contradict each other as well as that obtained from the new test: the new test is always corroborated by one or more of the old tests.

TABLE II.

No.	New 115° test.	Potassium- iodide- starch test.	Explosion test.	130° test.	Vieille test.
293 .....	Bad	Good	Bad	Good	Good
294 .....	Good	Bad	Good	Good	Good
326 .....	Bad	Good	Bad	Bad	Bad
344 .....	Bad	Good	Bad	Bad	Bad
396 .....	Good	Good	Bad	Good	Bad
405 .....	Bad	Good	Bad	Good	Bad
619 .....	Good	Bad	Bad	Good	Good
717 .....	Good	Good	Bad	Good	Bad
834 .....	Good	Good	Bad	Good	Bad

The new test has the following advantages over the old method:

- (1) The powder is tested in its natural condition.
- (2) It shows all products of decomposition; the old tests show only acid products, or, the Will test, only nitrogen.

(3) It shows the decomposition of nitro-compounds other than nitrocellulose which are often present in a finished powder, and it also shows the effect of this decomposition on the powder itself.

(4) It shows the effect on the stability of a powder, of small quantities of added substances (for masking stability or other purposes); volatile matter; handling and working which may set up local decomposition; traces of nitrating acids due to imperfect purification; decomposition due to saponification<sup>1</sup> by water, alkalis, carbonates, etc.

(5) It shows quantitatively the progress of all decomposition.

(6) The test itself, as well as the apparatus, is simple and not subject to variations like the old tests.

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## A STUDY OF THE DOUBLE CYANIDES OF ZINC WITH POTASSIUM AND WITH SODIUM.

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DURING the precipitation of gold and silver by means of metallic zinc, from the solutions obtained in the cyanide process of extracting precious metals from their ores, more or less zinc is dissolved and accumulates to a certain extent in these solutions, and its presence in some instances modifies or complicates the estimation of the simple alkaline cyanide in such solutions, and also slightly affects their subsequent action on some of the constituents of the ores or other materials treated by them.

A typical solution might have originally contained one-fourth of 1 per cent. of potassium cyanide, to which about the same amount of calcium hydroxide or sodium hydroxide might be added, after which, with occasional additions of the same reagents, it has been filtered alternately through pulverized ore and finely divided metallic zinc, several tenths of a per cent. of which might be found in the final solution. Some discussion has arisen as to the forms in which the zinc and cyanogen may be distributed in such a solution, whether, for instance, the zinc is in the form of a zincate ( $K_2ZnO_2$ ) or a double cyanide ( $K_2ZnCy_4$ ). The latter opinion has been more generally favored, but after a cyanide solution has been in use for some months—judging from the published analyses

<sup>1</sup> Thomas: *Ztschr. angew. Chem.*, (1899), p. 55.

of others as well as those made by the writer—the zinc will usually be found considerably in excess of the ratio of 1 atom zinc to 4 equivalents of cyanogen, that is, of the cyanogen contained in simple alkaline cyanides plus that in the double zinc cyanide, although the solution may still have an excellent solvent action on the precious metals and may still show the same percentage of “available” cyanogen by the usual methods of titration with silver nitrate, which was formerly supposed to indicate only that portion of the potassium cyanide which was uncombined with zinc and so available as a gold solvent.

A. James<sup>1</sup> proved that when equivalent weights of crystallized potassium zinc cyanide and caustic potash were mixed and evaporated, the crystals deposited were still almost pure double zinc cyanide and contained practically all the cyanogen present, and that the same compound separated out when potassium zincate was mixed with a potassium cyanide solution and evaporated. The writer has confirmed these results, and also found that almost any compound of zinc, dissolved in almost any proportion in potassium cyanide, will similarly deposit crystals of potassium zinc cyanide, proving that, *in saturated solutions*, this is the compound which tends to form, whether by virtue of greater stability or lesser solubility. In the dilute solutions met with in metallurgical work the conditions may be different, but it is difficult to prove, for instance, in a solution containing potassium, zinc, and cyanogen in the proportions corresponding to  $6K + Zn + 4Cy$ , whether it actually contains  $K_2ZnO_2 + 4KCy$  or  $K_2ZnCy_4 + 4KOH$ , as the results of titration or of gravimetric analysis would be the same in either case, and there seems to be no direct method of settling the question.

Some attempts were therefore made to decide this point by indirect means, to investigate more thoroughly the reactions which take place when various zinc compounds are dissolved in solutions of alkaline cyanides, or zinc cyanide in caustic alkalies, and to determine whether there is any appreciable difference in the effects of sodium and of potassium compounds in this direction, as might be inferred from the different constitutions assigned by Rammelsberg ( $K_2ZnCy_4$  and  $NaZnCy_3$ ) to the double cyanides of zinc with these metals. The results of the work in

<sup>1</sup> *J. Soc. Chem. Ind.*, 16, 120 (1897).

this connection on the solvent action of zinc potassium cyanide solutions on gold have been already published.<sup>1</sup>

#### METHODS OF ANALYSIS.

In the analyses necessary for this investigation the only determinations required were those of zinc, cyanogen, and alkali, carbonate being the only impurity present in quantity. In the crystals examined, water and alkali-metal were also weighed.

Water was estimated by heating the crystals to 110° C. until constant weight was attained.

Zinc was determined by decomposing with hydrochloric acid, heating to expel any hydrocyanic acid present, neutralizing with sodium hydroxide, then adding a constant quantity (3 cc.) of strong hydrochloric acid, diluting to 150 or 200 cc. and titrating with a weak solution of potassium ferrocyanide, using uranium acetate as indicator, the titration being carried out in a hot solution, and a correction (0.3 cc.) being deducted for the quantity necessary to color the indicator.

Cyanogen was estimated by dissolving in or adding ammonia, and titrating with standard silver nitrate, using potassium iodide as an indicator. When zinc was present, an excess of sodium hydroxide was also added, and when present in proportions approaching Zn:4Cy an addition of one part in 200 was made to the cyanogen found by titration, that correction having been found necessary by previous experiments.

Alkali (potassium or sodium cyanide or hydroxide) was titrated by standard sulphuric acid, using phenolphthalein as an indicator, or, in some cases, methyl orange. In most instances, excepting the earlier experiments, carbonates had been removed from the solutions by means of lime, and, when the alkalinity of simple alkali-metal cyanide was found to exceed that due to the cyanogen present, the slight excess of alkali was usually neutralized by addition of standard acid in small quantity.

Sodium and potassium were gravimetrically determined, in some instances, as sulphates.

The probable composition of the solutions was calculated as follows: If the zinc present exceeded the ratio Zn:4Cy all cyanogen was reckoned as  $K_2ZnCy_4$ , the remaining zinc as  $K_2ZnO_2$ , and residual potassium as KOH. If the zinc present were below the amount corresponding to the ratio Zn:4Cy, zinc was reckoned as  $K_2ZnCy_4$ ,

<sup>1</sup> *Eng. and Min. J.*, 64, 396, 426, 460.



the remaining cyanogen as  $\text{KCy}$ , and residual potassium as  $\text{KOH}$ . In the few cases in which zinc was in excess of the ratio  $\text{Zn} : 2\text{K}$ , the excess of zinc was calculated as  $\text{ZnCy}_2$  and the remainder as  $\text{K}_2\text{ZnCy}_4$  and  $\text{K}_2\text{ZnO}_2$ .

#### PREPARATION OF ZINC CYANIDE.

The standard methods recommended for its preparation are the precipitation of a zinc salt in solution by means of potassium cyanide (any carbonate in which coprecipitates zinc carbonate), and passing hydrocyanic acid into a solution of zinc acetate, when zinc cyanide separates. Special precautions are said to be necessary.<sup>1</sup>

According to Gmelin's "Handbook" the cyanide precipitated by the first method contains:

	From strong solutions. Per cent.	From weak solutions. Per cent.
$\text{ZnCy}_2$ .....	89.9	54.4
$\text{ZnO}$ .....	9.0	37.32
$\text{H}_2\text{O}$ .....	2.0	8.25
	<hr/> 99.9	<hr/> 99.97
Whence the percentage of the total zinc present		
in the form of $\text{ZnCy}_2$ is .....	87.2	50.2
in the form of $\text{ZnO}$ .....	12.8	49.8
and the approximate composition is	$7\text{ZnCy}_2 \cdot \text{ZnO}$	$\text{ZnCy}_2 \cdot \text{ZnO}$ .

Two attempts were made to prepare zinc cyanide by passing hydrocyanic acid into zinc acetate solution, but the amount of precipitate obtained was relatively small, and action seemed to cease at an early stage, presumably owing to the acetic acid set free preventing further action by the hydrocyanic acid, or redissolving the precipitate.

A 10 per cent. solution of purified zinc sulphate crystals was then precipitated by a 5 per cent. solution of "98 per cent. potassium cyanide" containing also sodium cyanide and carbonate, the zinc being kept in slight excess; the precipitate was washed free from sulphate. It was found to consist of a mixture of zinc cyanide with some zinc carbonate and a large proportion of zinc oxide or hydroxide.

<sup>1</sup> Gmelin's "Handbook," (1854 ed.), Vol. VII, p. 422; Corriol and Berthemet: *J. Pharm.*, 16, 444; *Br. Arch.*, 38, 153; *Repert.*, 36, 106; Bette: *Ann. Pharm.*, 31, 214; Henry: *J. Pharm.*, 18, 57; Schindler: *Mag. Pharm.*, 36, 67; Wittstein: *Repert.*, 63, 314; Rammelsberg: *Pogg. Ann.*, 42, 114; Joannis: *Compt. Rend.*, 92, 1338, 1417; Wohler: *Berz. Jahresl.*, 20, 152; Oppermann: *Jahresb. d. Chemis* (1860), p. 226; Varet: *Compt. rend.*, 108, 170; *Ann. chim. Phys.*, [7], 105 (1897).

A second lot was similarly prepared, but the cyanide was first carefully freed from carbonate by means of lime, and freshly boiled distilled water was used in dissolving and washing. This precipitate was found practically free from carbonate but only 58 per cent. of the zinc present was in the form of  $\text{ZnCy}_2$ , the remainder being presumably oxide or hydroxide. A third precipitation gave 55 per cent. of the zinc in the form of cyanide. In these and several other experiments it was found that the zinc cyanide lost cyanogen on washing, becoming more and more basic,<sup>1</sup> the wash-water smelling of hydrocyanic acid; after long washing, the zinc in the form of  $\text{ZnCy}_2$  approximated 50 per cent. of the total zinc present, indicating the composition  $\text{ZnO} \cdot \text{ZnCy}_2$ . This can be rapidly estimated by shaking up the precipitate, taking out two equal portions of the emulsion with a pipette (2 cc. if thick, or proportionately more if much water is present) and estimating zinc in one and cyanogen in the other by titration with ferrocyanide and silver nitrate respectively.

It is difficult to wash freshly precipitated zinc cyanide; it settles very slowly in water and will pass through any filter-paper; this may be remedied to some extent by adding about 5 per cent. of sodium sulphate to the first wash-waters, after which it settles fairly well, so that the water can mostly be decanted or siphoned off after five or ten minutes' standing.

On attempting to dry the precipitate there is always some decomposition, ammonia being formed for one thing; on allowing it to stand in the moist state, some ammonia is also developed.

The best results in preparation were obtained by first roughly precipitating a quantity of zinc cyanide by acting on zinc sulphate with carbonate-free alkaline cyanide; then adding to the roughly washed precipitate more alkaline cyanide—slightly in excess of the amount required to redissolve it. The resulting double cyanide solution was filtered clear, titrated to determine the amount of acid necessary to decompose the alkaline cyanide and liberate  $\text{ZnCy}_2$ , and then the whole was decomposed by a slight excess of sulphuric acid, added with constant stirring. The precipitation must be carried on in a good draft to avoid trouble with the hydrocyanic acid evolved. The vessel was then covered and allowed to stand till most of the precipitate had settled; the

<sup>1</sup> Although the reaction  $\text{ZnCy}_2 + \text{H}_2\text{O} = \text{ZnO} + 2\text{HCy}$  (dissolved) is said to absorb 13 to 16 heat units.

bulk of the clear liquor was poured off and the precipitate washed several times with water, the first one or two lots containing a little free acid. This insures the evolution or presence of some hydrocyanic acid and counteracts the tendency of the water to hydrolyze the cyanide and render it basic. In one case, the washing was conducted with a solution of hydrocyanic acid.

Prepared in this way the proportion, by weight, of zinc to cyanogen is almost exactly 5:4, or practically all the zinc is in the form of cyanide. The product thus obtained, kept as an emulsion, is alluded to as "pure zinc cyanide"; that obtained in earlier tests and approaching the composition  $\text{ZnO} \cdot \text{ZnCy}_2$  as "basic zinc cyanide."

#### PREPARATION OF PURE CRYSTALLIZED POTASSIUM ZINC CYANIDE,



This salt crystallizes readily in regular octahedra, and was easily prepared in solution by several methods.<sup>1</sup> It was obtained in a nearly pure form by first precipitating an impure basic cyanide by treating zinc sulphate with commercial "98 per cent." cyanide, containing about one-third sodium and two-thirds potassium cyanide, adding to the washed precipitate enough of the same cyanide in a hot solution to nearly redissolve it, filtering, cooling and allowing to crystallize, then recrystallizing the product three times by rapidly cooling a hot solution. The small crystals formed were thrown on a filter and sucked dry by a vacuum pump, washed twice with cold water and sucked dry; finally they were dried on filter-paper and kept some days over sulphuric acid. Water was estimated by drying at  $110^\circ \text{C.}$  to constant weight; on further heating there was no appreciable loss short of fusion. No sodium was detected.

	Calculated for $\text{K}_2\text{ZnCy}_4$ Per cent.	Found.				Average.
		I.	II.	III.	IV.	
Potassium....	31.56	31.49	....	....	...	31.49
Zinc .....	26.39	26.16	26.16	26.32	....	26.22
Cyanogen ....	42.05	41.88	41.88	41.77	41.77	41.82
Water .....	0.00	0.20	....	....	....	0.20
	100.00					99.73

The composition found by analysis, therefore, agrees precisely with

<sup>1</sup> Gmelin's "Handbook," Vol. VII, p. 422; Rammelsberg: *Pogg. Ann.*, 42, 112 (1837); Fresenius and Haidlin: *Ann. Chem. (Liebig)*, 43, 132; Sharwood: *Eng. Min. J.*, October 9, 1897; Schindler: *Mag. Pharm.*, 26, 67.

the percentage composition calculated from the formula assigned by Rammelsberg, whose determinations for zinc varied from 25.25 to 26.379.

#### SOLUBILITY.

This salt is stated in Comey's "Dictionary" to be "easily soluble in cold water." The mean of three determinations on the crystals above described gave a solubility of almost exactly 11 grams of potassium zinc cyanide in 100 cc. of water at a temperature of 20° C., but there is some tendency to form supersaturated solutions, and at higher temperatures the solubility is considerably greater. Only a minute trace was found to be dissolved by 100 cc. ethyl alcohol of specific gravity 0.798 (99 per cent.) at 20° C. In wood spirit, turpentine, ether, chloroform, acetone, carbon disulphide, coal oil and gasoline it was found to be completely insoluble.

On boiling a dilute water solution of this salt it is not precipitated, and carbonic acid is almost without effect upon the solution.

#### SODIUM ZINC CYANIDES, $\text{Na}_2\text{ZnCy}_4$ and $\text{NaZnCy}_4 + 2\frac{1}{2}\text{H}_2\text{O}$ .<sup>1</sup>

The only reference found to the double sodium-zinc cyanide was that of Rammelsberg,<sup>2</sup> also quoted by Gmelin's "Handbook," Vol. VII, p. 422.

Rammelsberg says, in effect: "It was prepared in the same way as the potassium salt (acting on zinc cyanide) by means of sodium cyanide. The latter was obtained by saturation of pure (strong) hydrocyanic acid with lime, and decomposition of the calcium cyanide with sodium carbonate. The solution of the double zinc (sodium) cyanide leaves first, on strong concentration, glittering white leaflets, the precise form of which could not be determined. The properties of this salt are in general those of potassium zinc cyanide, but it is very readily soluble in water, and holds water combined; this, however, it loses, as it seems completely, at 200° C. The loss of weight in two analyses shows 21.71 and 23.88 per cent.

"Analysis of the desiccated salt shows:

(1) 0.458 gram gave  $\text{ZnO}$  0.2194 =  $\text{Zn}$  0.17584;  $\text{Na}_2\text{SO}_4$  0.21 =  $\text{Na}$  0.068478.

(2) 0.51 gram gave  $\text{ZnSO}_4$  0.475 =  $\text{Zn}$  0.190695;  $\text{Na}_2\text{SO}_4$  0.26 =  $\text{Na}$  0.08478.

<sup>1</sup> In Morley and Muir's edition of Watts' "Dictionary," this formula is incorrectly quoted as  $\text{NaZnCy}_4 \cdot 5\text{H}_2\text{O}$ .

<sup>2</sup> *Pogg. Ann.*, 42, 112 (1837).

Whence the percentage is :

	Observed by Rammelsberg.		Calculated for NaZnCy <sub>2</sub> by Rammelsberg.	Recalculated for NaZnCy <sub>2</sub> . <sup>1</sup>
Zinc.....	38.593	37.391	38.65	39.26
Sodium.....	14.951	14.624	13.938	13.84
Cyanogen .....	not estimated		47.422	46.9
Cyanogen by difference (46.656) (47.985)			.....	....
			100.01	100.0

Or a compound of 2 equivalents zinc cyanide with 1 equivalent of sodium cyanide, with which 5 equivalents of water (HO in old atomic weights, *i. e.*, 2.5 molecules H<sub>2</sub>O in new system) appear to be combined, which would make 21.23 per cent. water. *The discrepancy between the found and calculated results lies doubtless in a small admixture of sodium carbonate which was always mixed with the salts examined.*"

#### ATTEMPTS AT PREPARATION OF SODIUM ZINC CYANIDE.

I made several preliminary attempts to obtain this salt by dissolving precipitated zinc cyanide, first in solutions prepared from the "purest" sodium cyanide on the market, and then with a solution of caustic soda saturated with HCN. The only crystals obtained were filmy flakes, left when the solutions had been evaporated to a thick syrup by standing several weeks in desiccators over sulphuric acid.

Larger quantities of a stronger solution were then prepared but these refused to crystallize at all until some of the flakes previously obtained were dropped in; this induced a slow deposition of similar leaf-like crystals, several grams of which were finally obtained, and dried by pressing between filter-paper. Analyses of these are given below as Samples A and B. On attempting to redissolve these in a little water, so as to recrystallize and purify them, they decomposed to some extent, an insoluble basic cyanide of zinc separating out in small quantity; the new solution could not be induced to crystallize. It was impossible to free them completely from the mother-liquor, which was so concentrated as to affect the analysis seriously.

Another solution was similarly prepared and allowed to stand over sulphuric acid for over a month without yielding any crystals; it was then left out of doors two days in severely cold weather, the temperature ranging from 0° to -35° C., when some large

<sup>1</sup> W. J. S.: F. W. Clarke's atomic weights.

tabular crystals were formed; these, however, turned out to consist chiefly of sodium carbonate with 56 per cent. of water, and further crops had a similar composition.

A larger quantity of sodium cyanide was obtained and similarly saturated with zinc cyanide, after removing all traces of carbon dioxide. After very long evaporation a number of octahedral crystals were found which yielded, by analysis, zinc, 27 per cent., cyanogen, 42.8 per cent., water, 1 per cent., proportions corresponding closely to those of  $K_2ZnCy_4$ , which they proved to be, resulting from a small amount of potassium found to have been present in the sodium cyanide used in this preparation.

In the meantime a number of experiments had been made which seemed to indicate the solution of zinc cyanide in practically equal amounts by equivalent quantities of potassium and sodium cyanide. These suggested the existence of the compound  $Na_2ZnCy_4$  in solution and in fact proved it so far as dilute solutions are concerned.

The ratio of zinc to cyanogen in the mother-liquor, from the first crop of crystals of sodium zinc cyanide, also corresponds to the existence of  $Na_2ZnCy_4$  in that concentrated solution. Although the sodium zinc cyanide crystals obtained and analyzed, both in this investigation and by Rammelsberg, were decidedly impure, still the atomic ratio of zinc to cyanogen is so nearly 1:3 as to make it almost certain that Rammelsberg's formula,  $NaZnCy_3$ , is correct. There must, however, remain some uncertainty as to the degree of hydration of this salt, as it very easily loses its water of crystallization. Rammelsberg stated that the water was expelled completely at 200° C. In my experiments it was found to lose all but 2 per cent. by drying over sulphuric acid *in vacuo* at about 20° C.; the greater portion of the water was lost at about 70° C., and there was only a trifling loss of weight when the material, dried at 110°, was heated to fusion.

The comparison given below of the composition calculated and found for the anhydrous compounds shows a considerable variation in different analyses, but a fair approximation to the atomic ratio  $Zn:3Cy$ .

	Percentage composition.						
	Water in cryst- als.	Anhydrous salt.			Atomic ratio.		
		Sodi- um.	Zinc.	Cyano- gen.	Water.	Sodi- um.	Zinc. Cyano- gen.
$\text{Na}_2\text{ZnCy}_4$ , calculated	....	21.3	30.3	48.3	...	2.0	1.0 4.0
$\text{NaZnCy}_2$ , calculated	....	13.84	39.26	46.9	...	1.0	1.0 3.0
Rammelsberg crys- tals, No. 1 .....	21.7	14.951	38.393	46.656	2.28	1.10	1.0 3.05
Rammelsberg crys- tals, No. 2 .....	22.88	14.624	37.391	47.958	2.34	1.11	1.0 3.22
W. J. S. sample A, dried over $\text{H}_2\text{SO}_4$ .	2.0	19.3	34.2	45.8	...	1.6	1.0 3.36
W. J. S. sample B, dried on filter- paper .....	26.0	...	33.8	42.57	2.41	..	1.0 8.16
W. J. S. sample C, second crop .....	23.6	...	35.5	42.4	2.4	..	1.0 3.0
Mother-liquor .....	...	...	...	...	..	..	1.0 4.0

The mother-liquor from crystals in samples A and B was of a syrupy consistency and had a specific gravity of about 1.35. One cubic centimeter was found to contain zinc, 205 milligrams, cyanogen, 327 milligrams, corresponding almost exactly to the ratio  $\text{Zn}:\text{4Cy}$ .

If the sodium is calculated to correspond to the ratio  $2\text{Na}:\text{Zn}$  we get 145 milligrams per cubic centimeter, or a total of 677 milligrams in 1 cc. or 1.35 grams of saturated solution, indicating that this salt,  $\text{Na}_2\text{ZnCy}_4$ , is soluble in its own weight of water.

#### METHOD OF CONDUCTING EXPERIMENTS ON THE ACTION OF POTASSIUM AND SODIUM HYDROXIDE AND CYANIDE UPON ZINC OXIDE AND CYANIDE.

The zinc cyanide was obtained in the form of an emulsion; by shaking this up and removing it with a pipette it was possible to gauge the quantity taken to within about 1 to 1.5 per cent., the material having been previously analyzed and being kept in a stoppered bottle. The zinc oxide was weighed out in most cases. The alkaline cyanide and hydroxide were kept in the form of fifth-normal solutions—double the strength intended for the experiments; except in preliminary experiments, the carbonate present was removed by addition of lime. Any slight excess of alkali in the cyanide solutions, due to hydroxide, was usually neutralized by the addition of standard sulphuric acid, the alkaline sulphate thus formed not interfering with the results.

In any series of experiments a number of graduated flasks were taken, and with a pipette of half their capacity they were half-filled with the fifth-normal solution of cyanide or hydroxide of potassium or of sodium. Water was then added to partly fill the remaining half of the flask, then the zinc oxide was added, or the zinc cyanide run in from a pipette in suitable amount; then water was added to fill the vessel to the mark (or slightly above the mark when the solid was added in large excess); the contents were thoroughly shaken, and allowed to stand with occasional shaking for some hours or days, either in the cold or with occasional heating. The contents were finally allowed to settle, and aliquot portions of the clear solution were removed with a pipette for analysis; zinc and cyanogen alone were determined, as it had been found that no alkali-metal was removed from the solution. In some instances the solutions were filtered off, in order to allow of examining the precipitates.

In the analyses the volumetric solutions were adjusted to some multiple of normal strength, and the weights of alkali-metal, zinc, or cyanogen, were not calculated but are stated as so many atoms, molecules, or equivalents per 100 cc. of solvent used, the solvent being decinormal in every case. One "atom," "equivalent," etc., as thus used, means the corresponding weight expressed in tenths of milligrams. In the tables, therefore, one can at once read, from the experimental data, the number of atoms of zinc, for instance, which passed into solution in a particular experiment, by the action of 100 molecules of alkaline cyanide or hydroxide.

SOLVENT ACTION ON GOLD OF SOLUTIONS OF POTASSIUM ZINC  
CYANIDE.

This is less than that of a solution of simple potassium cyanide containing the same amount, or one-half the amount, of cyanogen in equal volumes.

*It is increased by addition of caustic alkali, other conditions remaining the same, and the increase is greatest in those solutions to which oxygen has the freest access.*

*The considerable increase in solvent power observed when caustic potash is added (always providing that oxygen is accessible), coupled with the superior effect of free potassium cyanide, is good evidence that some free potassium cyanide is formed upon such addition, and therefore that in dilute solutions potassium zinc*



*cyanide is partially decomposed by caustic alkali, with formation of simple alkaline cyanide, in accordance with the principles of chemical equilibrium between substances in solution.*

ACTION OF DILUTE SOLUTIONS OF ALKALINE HYDROXIDES ON ZINC OXIDE.

This must be considered in connection with the side-reactions involved in the solution of zinc oxide in alkaline cyanides, or of zinc cyanide in alkaline hydroxide solutions, as will be shown later.

Prescott and Wilson<sup>1</sup> have shown that 8 molecules of potassium hydroxide, in a solution of *normal* strength, are necessary to precipitate and redissolve 1 molecule of zinc chloride or other zinc salt, and that 7 molecules of sodium hydroxide produce the same effect. Therefore 6 molecules of potassium hydroxide, or 5 of sodium hydroxide, are the least quantities which, in a normal solution, can dissolve freshly precipitated zinc hydroxide. The solutions must then contain:  $K_2ZnO_3 + 4KOH$ , or  $Na_2ZnO_3 + 3NaOH$ .

*Heating or great dilution decomposed or dissociated these compounds, precipitating zinc oxide, but by cautious addition of acid all the excess of alkali could be neutralized, and alkaline zincate left.*

In a more dilute, such as a decinormal, solution I have found the amount of zinc oxide dissolved per unit of alkali very much smaller, especially when a dry oxide is used, but that by careful neutralization the zincate may be left in solution if a very slight amount of free alkali is allowed to remain. The solution, however, is always precipitated on heating unless a considerable excess of free alkali is present.

DECINORMAL SOLUTIONS OF ALKALINE HYDROXIDES WITH ZINC OXIDE.

On leaving an excess of dry, finely divided, zinc oxide in contact with solutions of sodium and potassium hydroxides, both of tenth-normal strength, for several days, during which time they were frequently agitated, the amounts found in solution were as follows:

<sup>1</sup> This Journal, 2, 27.

Potassium hydroxide, decinormal solution :

(1) Cold : 100 molecules potassium hydroxide dissolved 2.1 molecules zinc oxide.

(2) Cold : 100 molecules potassium hydroxide dissolved 2.7 molecules zinc oxide.

(3) Heated gently : 100 molecules potassium hydroxide dissolved 2.5 molecules zinc oxide.

Sodium hydroxide, decinormal solution :

(1) Cold : 100 molecules sodium hydroxide dissolved 4.5 molecules zinc oxide.

(2) Warmed : 100 molecules sodium hydroxide dissolved 8.3 molecules zinc oxide.

On boiling, either of the above solutions, a slight precipitate was thrown down.

The only importance of these last experimental results is to show how little tendency there is for the alkaline zincates to form in these dilute solutions, and how easily they are decomposed.

#### ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM CYANIDE UPON ZINC CYANIDE.

The results are given in Table I. In Nos. 1 to 4 the potassium cyanide contained some sodium cyanide and a little carbonate; the zinc cyanide was also basic. In Nos. 5 to 9 the zinc cyanide was almost exactly normal, but in 5 to 8 it had been kept several days and may have commenced to decompose with the formation of ammonia compounds.

#### ACTION OF A DILUTE (DECINORMAL) SOLUTION OF SODIUM CYANIDE UPON ZINC CYANIDE.

The sodium cyanide used contained a little free alkali, but only traces of other impurities. The zinc cyanide was almost normal and recently prepared: 5 cc. of the emulsion contained approximately 19 mol.  $\text{ZnCy}_2$  + 1 mol.  $\text{ZnO}$ .

The ratio of zinc to cyanogen in the saturated solutions closely approximates 1 atom to 4. The solution appears to have followed very closely the reaction corresponding to  $4\text{NaCy} + \text{ZnCy}_2 = \text{Na}_4\text{ZnCy}_4$ , and it is, therefore, probable that the salt  $\text{Na}_4\text{ZnCy}_4$ , analogous to the corresponding potassium compound, is formed and exists in these dilute solutions. Increasing the proportion of zinc cyanide beyond that indicated in the equation has no appreciable effect, the excess remaining practically unacted upon.

TABLE I.— $\text{KCN} + \text{Zn}(\text{CN})_2$ .

Experiment No. Materials:	1. Commercial "98 per cent." Basic	2. zinc	3. potassium cyanide	4. potassium cyanide	5. Merck's purest potassium cyanide	6. Pure	7. zinc	8. potassium cyanide	9.
Solvent contained in 100 cc.:									
Equivalents Cy.....	100	100	100	100	100	100	100	100	100
Atoms K (+ Na in 1-4) ....	108.2	108.2	108.2	108.2	100	100	100	100	100
Zinc cyanide used:	Excess	Excess	Slight excess	Large excess	25 mol.	50 mol.	100 mol.	200 mol.	Large excess.
Treatment:	Cold	Heated occasionally	Cold	Warmed occasionally	Cold	Cold	Cold	Cold	Cold
Hours of contact.....	48	48	170	170	120	120	120	120	48
Residue <sup>1</sup> or precipitate....	Moderate	Moderate	Slight	Large	None	Slight	Moderate	Large	Large
Solution analysis: 100 cc. were found to contain:									
Equivalents Cy.....	211	210	200	197	140	201.0	212	218	202
Atoms Zn .....	61.0	59.8	53.7	53.2	26.0	50.1	55.5	56.0	50.2
Composition calculated: molecules per 100 cc.:									
$\text{K}_2\text{ZnCy}_4$ .....	49.25	49.65	50.0	49.2	26.0	50.0	50.0	50.0	50.0
$\text{K}_2\text{ZnO}_3$ .....	4.85	4.45	3.7	4.0	0	0	0	0	0
$\text{ZnCy}_2$ , in excess of $\text{K}_2\text{ZnCy}_4$	7.0 <sup>2</sup>	5.7 <sup>2</sup>	0	0	0	0.1	5.5	6.0	0.2
Cy not accounted for.....	....	....	0.8 KOH	1.8 KOH	36 KCy	....	....	....	....
	....	....	....	....	....	0.8	1.0	6.0	1.6

<sup>1</sup> The composition of the precipitates was examined in the case of Nos. 7 and 8; there was found for each 100 cc. of solution obtained: In No. 7, Zn 20 atoms, Cy 37 equivalents; = 18.5  $\text{ZnCy}_2$ , 1.5  $\text{ZnO}$ .

In No. 8, Zn 99.5 atoms, Cy 198 equivalents; = 99  $\text{ZnCy}_2$ , 0.5  $\text{ZnO}$ .

The amounts thus found do not account for all the zinc cyanide left undissolved, as only about two-thirds of the residues could be retained by filtration; they prove, however, that the composition of the undissolved portion was practically unaltered. The reaction is undoubtedly  $4\text{KCy} + \text{ZnCy}_2 = \text{K}_2\text{ZnCy}_4$ , complicated slightly by impurities. The excess of cyanogen and of zinc in some cases is probably due to small amounts of ammonium compounds developed in the zinc cyanide.

<sup>2</sup> In Nos. 1 and 2 the solutions were opalescent, a little zinc cyanide remaining in suspension.

TABLE II.—NaCN + ZnCy<sub>2</sub>.

Experiment No.	1.	2.	3.
Solvent contained in 100 cc.:			
Equivalents Cy .....	100	100	100
Atoms Na .....	108.3	108.3	108.3
Zinc cyanide used :			
Cc. emulsion .....	5.0	15.0	25.0
Molecules ZnCy <sub>2</sub> .....	19.0	57.0	95.0
Molecules ZnO .....	1.0	3.0	5.0
Hours of contact .....	24.0	120.0	120.0
Solution analysis, found in 100 cc.:			
Equivalents Cy .....	...	200.5	202.0
Atoms zinc .....	...	50.2	51.0
Residue .....	None	Moderate	Heavy
Residue analysis, per 100 cc. solution :			
Equivalents Cy .....	0	9.0	82.0
Atoms Zn .....	0	5.0	42.0
Composition calculated : molecules per 100 cc. of solution :			
In solution : Na <sub>2</sub> ZnCy <sub>4</sub> .....	20.0	50.1	50.5
Na <sub>2</sub> ZnO <sub>2</sub> .....	0.0	0.1	0.5
NaOH .....	10.3	8.1	6.3
NaCy in excess .....	58.0	0.0	0.0
In residue : ZnCy <sub>2</sub> .....	0.0	4.5	41.0
ZnO .....	0.0	0.5	1.0

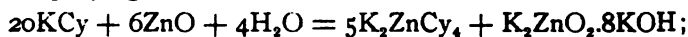
ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM CYANIDE UPON ZINC OXIDE.

In all but the first four experiments, the results of which are given in Table III, the potassium cyanide solution was free from carbonate, and the small amount of free alkali found was carefully neutralized by addition of standard sulphuric acid. A residue was left in every case but that in No. 7 was excessively small. The residue was tested in several instances, and proved to be zinc oxide holding a mere trace of cyanogen.

Examining the results obtained with cold solutions it will be seen that they all correspond closely to the equation:



or, simplifying,



that is to say, that the potassium cyanide is apparently completely converted into the double zinc potassium cyanide, with formation of potassium hydroxide, which dissolves a further portion of zinc oxide. After calculating all the cyanogen in solution to K<sub>2</sub>ZnCy<sub>4</sub>,

TABLE III.—KCN + ZnO.

Experiment No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
Materials .....	Comm'l "99" KCN (+ NaCN). Dense finely powdered ZnO.					Merck C.P. KCN. Fresh Zn(OH) <sub>2</sub>		Merck's C.P. KCN. Baker & Adamson's C.P. ZnO, very finely divided.				"V. H. P. KCN," nearly pure. Merck's C.P. ZnO, very finely divided.				
Solvent contained in 100 cc.:																
Equivalents Cy	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Atoms K.....	108.2	108.2	108.2	108.2	108.2	100	100	100	100	100	100	100	100	100	100	100
Zinc oxide	Slight	Large	Slight	Large	Ex-	Ex-	20	35	70	70	70	48	50	100	48	100
added.....	excess	excess	excess	excess	cess	cess	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.	mol.
Treatment.....	Cold	Cold	Boiled	Boiled	Cold	Heated	Cold	Cold	Cold	Heated	Heated	Heated	Cold, often	Heated	Heated	gently
Hours contact			occ'a'y	occ'a'y		occ'a'y				occasionaly.			shaken.			continuously.
before testing	48	48	48	48	48	48	48	120	120	48	48	36	36	36	36	36
Solution analysis; 100 cc. were found to contain:																
Equivalents Cy	100.5	100.0	100.2	100.0	(100) <sup>1</sup>	(100) <sup>1</sup>	(100) <sup>1</sup>	99.8	100.1	100	(100) <sup>1</sup>	98.0	99.2	100.0	94.0 <sup>2</sup>	93.0 <sup>2</sup>
Atoms zinc....	27.6	31.6	28.2	29.5	32.0	33.1	20.0	30.4	30.6	28.5	28.2	29.8	29.7	29.7	27.9	27.6
Composition calculated; molecules per 100 cc.:																
K <sub>2</sub> ZnCy <sub>4</sub> .....	25.1	25.0	25.05	25.0	25.0	25.0	20.0	24.95	25.02	25.0	25.0	24.5	24.8	25.0	23.5	23.2
K <sub>2</sub> ZnO <sub>3</sub> .....	2.5	6.6	3.2	4.5	7.0	8.1	0.0	5.45	5.58	3.5	3.2	5.3	4.9	4.7	4.4	4.4
KOH.....	53.0	45.0	51.7	48.8	36.0	33.8	40	39.2	38.8	43.0	43.4	40.4	40.6	40.6	44.2	44.8
KCy.....	0.0	0.0	0.0	0.0	0.0	0.0	20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

<sup>1</sup> Assumed.<sup>2</sup> Loss of cyanogen due probably to continuous heating.

the residual potassium and zinc correspond very closely to the composition  $K_2ZnO_3.8KOH$ , which agrees with the finding of Prescott and Wilson,<sup>1</sup> that 8 molecules of potash are necessary in a *normal* solution to precipitate and redissolve 1 molecule of zinc oxide, corresponding to  $K_2ZnO_3.4KOH$  in a solution of *normal* strength, while a larger excess of alkali is required for solution in a weaker solution, such as the decinormal solution used in these experiments.

ACTION OF A DILUTE (DECINORMAL) SOLUTION OF SODIUM CYANIDE  
UPON ZINC OXIDE.

The sodium cyanide used was of the very highest purity, it was freed from carbonates by lime-water, and the slight amount of free alkali remaining was neutralized by standard sulphuric acid. The zinc oxide was Merck's chemically pure, prepared by a dry process, and was very finely divided. Contact was maintained for about thirty-six hours, during the first twenty-four of which the mixtures were frequently shaken.

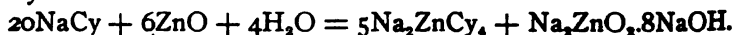
TABLE IV.— $NaCN + ZnO$ .

Experiment No.	1.	2.	3.	4.	5.	6.
Solvent contained in 100 cc.:						
Equivalents Cy ....	100	100	100	100	100	100
Atoms Na .....	100	100	100	100	100	100
Zinc oxide added in molecules .....	25	50	75	100	50	100
Treatment .....	Cold	Cold	Cold	Cold	Warmed	Warmed
Found in resulting solution per 100 cc.:						
Equivalents Cy ....	100.5	100.0	..	..	100.0	99.0
Atoms zinc .....	23.2	30.0	30.0	30.3	28.5	28.8

A residue was left in every case but No. 1, in which all but a mere trace of the oxide had dissolved.

From the very close agreement of the ratio between the zinc found in solution and the solvent taken, with the similar ratio observed in the case of potassium cyanide solutions acting on zinc oxide, it is evident that the reactions in the two cases are practically identical. The calculation of the molecular composition of the resulting solution has, therefore, been omitted.

The ratio evidently corresponds to the reaction between 20 molecules  $NaCy$  and 6 molecules  $ZnO$ , and the equation corresponding may be stated:



<sup>1</sup> This Journal, 2, 27.

ACTION OF COLD DILUTE (DECINORMAL) SOLUTIONS OF POTASSIUM HYDROXIDE UPON ZINC CYANIDE.<sup>1</sup>

The potassium hydroxide used was freed from carbonate, and the zinc cyanide was nearly normal and recently prepared.

From the experimental results which are tabulated in Table V it appears that zinc cyanide is dissolved readily and permanently by a decinormal solution of potassium hydroxide, up to the point corresponding to the proportion  $2\text{KOH} + \text{ZnCy}_2$ ; further additions dissolve less readily up to the point of saturation, which occurs when the number of molecules of zinc cyanide added approaches that of the potassium hydroxide; any zinc cyanide in excess of the proportion  $\text{ZnCy}_2 + \text{KOH}$  is unacted upon. If the solution has been thus saturated with zinc cyanide, or if the amount dissolved exceeds the proportion 1 molecule  $\text{ZnCy}_2 + 2$  molecules  $\text{KOH}$ , then a precipitate soon begins to form and continues to fall out for some time, or until equilibrium is reached; this precipitate consists of pure zinc oxide, which is deposited in a finely divided form and adheres closely to the sides of the containing vessel.

If the mixture is warmed, the precipitation is hastened and equilibrium is soon reached. In any case, the *final* solution approaches the composition  $\text{K}_2\text{ZnCy}_4$ , but in cases where the zinc cyanide is but slightly in excess of the proportion  $\text{ZnCy}_2 + 2\text{KOH}$ , an appreciable amount of potassium zincate seems to remain in solution unless heat is applied, when it soon decomposes with deposition of zinc oxide.

The complete reaction, *when zinc cyanide is in excess and after equilibrium has been attained*, approaches that represented by the equation  $2\text{KOH} + 2\text{ZnCy}_2 = \text{K}_4\text{ZnCy}_4 + \text{ZnO} + \text{H}_2\text{O}$ . If, however, the potassium hydroxide is in excess, the reaction appears to be  $4\text{KOH} + 2\text{ZnCy}_2 = \text{K}_2\text{ZnCy}_4 + \text{K}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$ . If the proportion of molecules of hydroxide to zinc cyanide lies between 1:1 and 2:1, there appears to be a mixed reaction, involving both of the above equations.

The composition assigned by calculation to the various solutions examined, as regards proportion of potassium zinc cyanide and potassium zincate, is verified by the behavior of these solutions on heating, those in which the larger proportions of zincate are indicated depositing the heavier precipitates of zinc oxide.

<sup>1</sup> See Curves A. and B.

TABLE V.—KOH + ZnCy<sub>2</sub>.

Experiment No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Molecules KOH in 100 cc. of solvent	100	100	100	100	100	100	100	100	100	100
Molecules ZnCy <sub>2</sub> added.....	13	26	42	52	52	78	100	100	125	250
Effect.....	Dissolved completely									
On standing .....	12 hrs. 2 hrs., slight very pp., slight verulent, forms slowly. flocc't pp.									
Effect of boiling a portion of clear supernatant solution <sup>1</sup> .....	Heavy pp. Heavy pp. Heavy pp. Moderate pp. Slight pp. in 2 min. Slight pp. in 5 min. No pp.									
Solution analysis ; 100 cc. were found to contain :										
Equivalents Cy . .	25.6	52.0	81.2	100.5	104.2	157.1	192.4	197.0	205.5	207.0
Atoms Zn .....	12.95	26.2	38.9	40.04	38.1	47.0	54.1	55.8	57.6	59.0
Residue and precipitates found per 100 cc. of solution :										
Equivalents Cy ...	0	0	1.0	1.0	1.0	2.0	15.0	15.0	45.0	290.0
Atoms Zn .....	0	0	8.66	13.0	16.6	20.6	46.4	52.0	64.3	190.0
Composition calculated : molecules per 100 cc. of solution ; in solution :										
K <sub>2</sub> ZnCy <sub>4</sub> .....	6.4	13.0	20.3	25.13	26.05	39.3	46.05	46.35	47.6	47.25
K <sub>2</sub> ZnO <sub>3</sub> .....	6.55	13.2	18.6	14.9	12.05	7.7	3.95	3.65	2.4	2.75
KOH free .....	74.1	43.6	22.2	19.92	23.8	6.0	0	0	0	0
ZnCy <sub>2</sub> .....	0	0	0	0	0	0	4.1	5.8	7.6	9.0
In residue and precipitate :										
ZnCy <sub>2</sub> .....	0	0	0.5	0.5	0.5	1.0	7.5	7.5	22.5	145.0
ZnO .....	0	0	8.16	12.5	16.1	19.6	39.0	44.5	41.8	45.0

1 In one case (No. 8) the solution was examined after heating and found to contain, per 100 cc., 106 equivalents Cy, 50.1 atoms Zn, corresponding to a composition of 49 molecules K<sub>2</sub>ZnCy<sub>4</sub> and 1 molecule K<sub>2</sub>ZnO<sub>3</sub>. The solution had the characteristic sweet taste of potassium zinc cyanide, slightly modified by the free alkali present.

<sup>1</sup> In one case (No. 8) the solution was examined after heating and found to contain, per 100 cc., 196 equivalents Cy, 50.1 atoms Zn, corresponding to a composition of 49 molecules K<sub>2</sub>ZnCy<sub>4</sub> and 1 molecule K<sub>2</sub>ZnO<sub>3</sub>. The solution had the characteristic sweet taste of potassium zinc cyanide, slightly modified by the free alkali present.

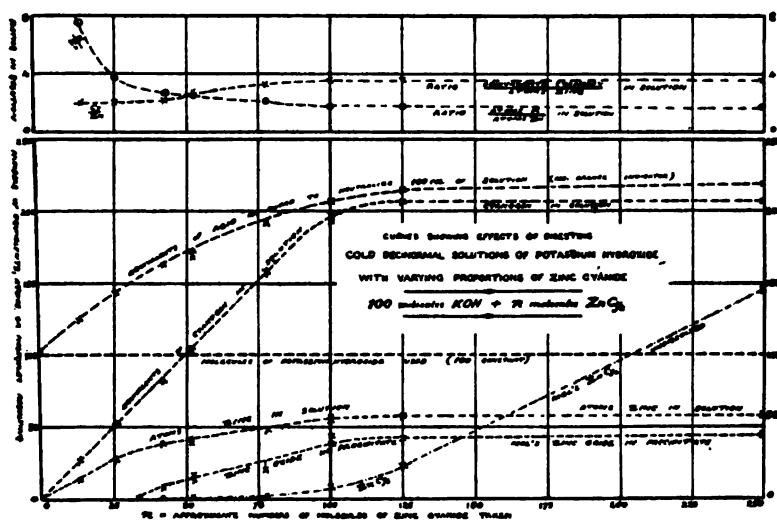


The reaction taking place when the larger proportion of zinc cyanide passes into unstable solution—1 molecule of zinc cyanide for 1 molecule of hydroxide of either potassium or sodium as shown in tables V and VI—may possibly be accounted for by the formation (in the latter case) of the unstable compounds  $\text{NaZnCy}_3$ ,<sup>1</sup> and  $\text{Na}_2\text{Zn}_2\text{O}_3$ ,<sup>2</sup> and possibly  $\text{KZnCy}_3$  and  $\text{K}_2\text{Zn}_2\text{O}_3$ ,<sup>3</sup> in the former,



the latter compounds splitting up to form  $3\text{Na}_2\text{ZnCy}_4 + 3\text{ZnO}$ . This is suggested as a probable explanation of the instability of the solutions thus formed, the compounds  $\text{K}_2\text{Zn}_2\text{O}_3$  and  $\text{Na}_2\text{Zn}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (or  $\text{NaHZnO}_2$ ) being stated by their discoverers to be decomposed by water, while from the experiments already described it appears that  $\text{NaZnCy}_3$  is obtained only in concentrated solutions.

The curves appended show more clearly the variation in composition found with addition of varying proportions of zinc cyanide and constant quantities of potassium hydroxide. Curve A indicates the results directly obtained by analysis of solutions and residues, while Curve B shows the molecular proportions of double cyanide, zincate, and other products calculated therefrom.

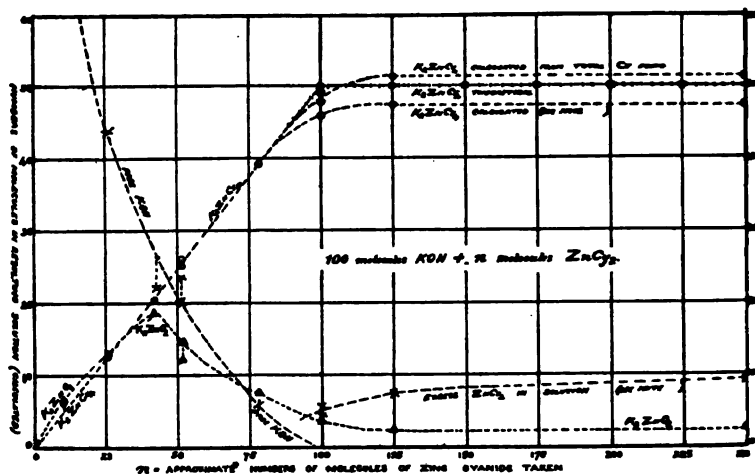


Curve A. Fig. 1.

<sup>1</sup> Rammelsberg: *Pogg. Ann.*,

<sup>2</sup> Comey and Jackson: *Am. Chem. J.*, 11, 145.

<sup>3</sup> Fremy: *Compt. rend.*, 18, 116.



Curve B. Fig. 2.

The fact that in some cases, especially when the proportion of zinc cyanide was very large, the amounts of zinc and of cyanogen finally found in the solution were somewhat in excess of those corresponding to the formation of  $K_2ZnCy_4$ , may be explained either by the dissolving of some  $ZnCy_2$  as such, or by its forming a certain proportion of  $KZnCy_3$ , which remains undecomposed, but the most probable explanation is the formation of a small amount of ammonia in the zinc cyanide, either before or during the experiments, 3 molecules of ammonia having been found to dissolve 1 molecule of zinc cyanide, when applied in dilute solution.

#### ACTION OF DILUTE (DECINORMAL) SOLUTIONS OF SODIUM HYDROXIDE UPON ZINC CYANIDE.

The general effects on mixing zinc cyanide with sodium hydroxide were similar to those with potassium hydroxide. The zinc cyanide dissolved readily on the first additions, then more slowly until the number of molecules of zinc cyanide dissolved approached that of the sodium hydroxide, when the solution became saturated: on standing, such a saturated solution deposited about half the dissolved zinc as oxide. In the final solution, however, the proportion of cyanogen present to sodium hydroxide taken is smaller than is the case with an equivalent amount of potassium hydroxide, when an excess of zinc cyanide is used, *viz.*, about 180

TABLE VI.—NaOH + ZnCy<sub>2</sub>.

Experiment No. Materials :	1.	2.	3.	4.	5.	6.	7.
	Caustic soda with a little carbonate	Basic zinc cyanide			Pure caustic soda	Pure zinc cyanide	
Solvent contained in 100 cc.							
NaOH in molecules.....	100	100	100	100	100	100	100
Zinc cyanide added .....	Slight excess	Slight excess	Large excess	Large excess.	82 mola.	102 mola.	136 mola.
Treatment.....	Cold	Cold	Cold	Warmed occasionally	Cold	Cold	Cold
Effect.....	Dissolved completely	Dissolved except trace	Considerable residue	Much residue	Dissolved completely	Dissolved except trace	Much residue
On standing .....	Slight pp.	Pp. slowly formed	Heavy pp.	Heavy pp.	Pp. slowly formed	Heavy pp.	Heavy pp.
Cyanogen in pp. or residue.....	None	Trace	Much	....	Trace	....	Much
Effect of boiling a portion of clear supernatant solution .....	Pp. finally very heavy	Slight pp.	Slight pp. after time	Very slight pp.	Slight pp.	Slight pp.	Very slight pp.
Solution analysis : 100 cc. were found to contain :							
Equivalents Cy.....	137.0	177.0	183.0	166.0	165.0	181.0	184.0
Atoms Zn .....	44.0	50.0	53.8	41.5	48.6	49.6	51.0
Composition calculated : molecules per 100 cc. solution :							
Na <sub>4</sub> ZnCy <sub>4</sub> .....	34.25	44.25	43.85	41.5	41.25	45.25	45.5
Na <sub>2</sub> ZnO <sub>2</sub> .....	9.75	5.75	6.15	0.0	7.35	4.35	4.5
NaOH free .....	12.0	0.0	0.0	17.0	2.8	0.8	0.0
ZnCy <sub>2</sub> in excess.....	0.0	0.0	3.8	0.0	0.0	0.0	1.0

equivalents cyanogen to 100 of soda, as against about 200 cyanogen to 100 of potash.

The extent of precipitation upon heating the clear solutions agrees in a general way with the proportion of zincate calculated when the cyanogen is reckoned as  $\text{Na}_2\text{ZnCy}_4$ , but not when it is reckoned as  $\text{NaZnCy}_2$ .

It will be noted that the values for  $\text{Na}_2\text{ZnCy}_4$ , etc., in Nos. 5, 6, and 7 fit within 1 or 2 units of those plotted in Curve B for  $\text{K}_2\text{ZnCy}_4$  on the parallel experiments with KOH. Compare also Table V.

After heating, the solution was examined only in the case of No. 6, the analysis of which showed 181 equivalents cyanogen and 46 atoms zinc, corresponding to 45.25 molecules  $\text{Na}_2\text{ZnCy}_4$ , as before, 0.75 molecule  $\text{Na}_2\text{ZnO}_2$ , and 8 molecules NaOH, which would indicate the stability of the compound  $\text{Na}_2\text{ZnCy}_4$ , confirmed also by the results of No. 4, the unstable sodium zincate being almost completely decomposed by the heating.

The length of time of contact in experiments 1 to 4 was not recorded but was at least three to four days; in Nos. 5 to 7 it was forty-eight hours.

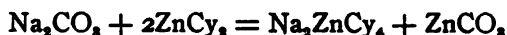
#### ACTION OF SODIUM CARBONATE SOLUTION ON ZINC CYANIDE.

A solution of sodium carbonate of known strength and volume was mixed with a considerable quantity of basic zinc cyanide. Two such mixtures were made, each was placed in a graduated vessel and water added till the total volume in each was such that 100 cc. contained 20 milligram-molecules (200 mols)  $\text{Na}_2\text{CO}_3$ . These mixtures were left for forty-eight hours. No. 1 was kept cold, but shaken at intervals. No. 2 was heated to boiling-point for about two minutes at the start, and again after twenty-four hours, and also shaken occasionally. After forty-eight hours zinc and cyanogen were estimated in the clear solutions.

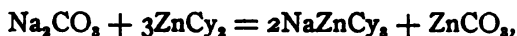
The character of the semi-transparent, gelatinous, zinc cyanide changed soon after being introduced, very rapidly on warming, becoming dead-white and bulky,—resembling zinc carbonate, which was probably formed in part. The residue settled slowly but was *very easily filtered off*. A little gas was given off from No. 2 after heating.

	No. 1. Cold.	No. 2. Heated.
Treatment (48 hours).....		
100 cc. contain finally :		
Atoms Na (from solvent) .....	400.0	400.0
Atoms Zn (dissolved).....	49.8	72.0
Equivalents Cy (dissolved).....	144.0	236.0
Ratio Cy/Zn.....	2.9	3.3
Ratio Na/Zn .....	8.0	5.5
Ratio Cy/Na .....	0.36	0.59

There seems to have been no complete reaction. According as  $\text{Na}_2\text{ZnCy}_4$  or  $\text{NaZnCy}_3$  were formed (see sodium zinc cyanide above), one would expect a reaction such as illustrated by the equation



or



as zinc carbonate is evidently one of the products. The latter reaction (forming  $\text{NaZnCy}_3$ ) is apparently suggested by the ratio of the zinc and cyanogen, but the ratios of both zinc and cyanogen to sodium are so small as to make it certain that much of the sodium carbonate remained undecomposed.

The resulting clear solution acted as a solvent for gold.

#### SUMMARY OF RESULTS.

When an alkaline solution, containing potassium, zinc and cyanogen, is concentrated, potassium zinc cyanide ( $\text{K}_2\text{ZnCy}_4$ ) readily crystallizes out and can be easily obtained in a state of considerable purity. This salt is also formed in solution when potassium cyanide acts on zinc cyanide or zinc oxide, or when potassium hydroxide acts upon an excess of zinc cyanide, as, when equilibrium is attained, and any zincate formed is decomposed by heating the atomic ratio of zinc to cyanogen in the solution is almost exactly 1:4.

A sodium cyanide solution, saturated with zinc cyanide and concentrated, crystallizes with extreme difficulty to form hydrated crystals of sodium zinc cyanide ( $\text{NaZnCy}_3$ ) which it seems impossible to obtain pure, and which decompose to some extent on addition of water, precipitating basic zinc cyanide. This salt does not appear to exist in the solution, as the mother-liquor contains zinc and cyanogen in approximately the ratio of 1:4. Also when dilute solutions of sodium cyanide act on zinc cyanide or oxide, or sodium hydroxide on an excess of zinc cyanide, the atomic ratio

of zinc to cyanogen in the resulting solution is approximately 1:4, so that the compound  $\text{Na}_2\text{ZnCy}_4$  is contained both in dilute and concentrated solutions.

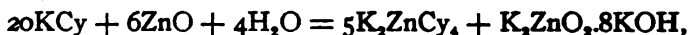
The hydroxides of potassium or sodium, in decinormal solution, dissolve very little zinc oxide when agitated with it; the zincate formed is largely decomposed on boiling, depositing zinc oxide, even in the presence of a large proportion of alkali.

Potassium cyanide, in dilute solution, dissolves zinc cyanide in accordance with the equation

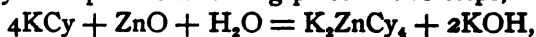


forming a stable solution, little affected by long boiling or by the presence of carbonic acid. In dilute solutions, sodium cyanide appears to follow a similar reaction with zinc cyanide,  $2\text{NaCy} + \text{ZnCy}_2 = \text{Na}_2\text{ZnCy}_4$ , but on concentrating the solutions the formation of the crystals of a different compound indicates that the reaction  $\text{NaCy} + \text{ZnCy}_2 = \text{NaZnCy}_3$  takes place under certain conditions.

Potassium cyanide, in decinormal solution, dissolves small proportions of zinc oxide completely. When the zinc oxide is present in excess, it is dissolved in the proportion of 3 molecules of zinc oxide for 10 molecules of potassium cyanide, agreeing with the equation



which may be explained as taking place in two steps,



the potassium hydroxide further reacting,



On boiling the solution of mixed double cyanide and zincate, the latter is partially decomposed with precipitation of zinc oxide.

With dilute solutions of sodium cyanide, the effects upon zinc cyanide are precisely similar to those observed with potassium cyanide under similar conditions.

Dilute solutions of potassium hydroxide dissolve zinc cyanide. If the zinc cyanide is in less than the proportion corresponding to  $\text{ZnCy}_2 + 2\text{KOH}$ , it is dissolved completely and permanently:



although upon heating the solution most of the zincate is decomposed with precipitation of zinc oxide, leaving free alkali in solution. Zinc cyanide is also completely dissolved in proportions

up to that of  $\text{ZnCy}_2 + \text{KOH}$ , but a precipitate of zinc oxide begins shortly to fall out. Any zinc cyanide in excess of the last proportion stated is unaffected by the solvent.

When the zinc cyanide corresponds to, or is in excess of, the proportion of 1 molecule to 1 of hydroxide, it is dissolved in that proportion, but one-half of the zinc separates out as oxide, the separation beginning soon after solution, and going on slowly. The complete reaction, with an excess of zinc cyanide, and after equilibrium has been attained by the separation of oxide, agrees with the equation



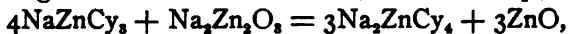
When a very large excess of zinc cyanide had been added, the zinc and cyanogen in solution sometimes slightly exceeded the proportions indicated by this equation, probably owing to the development of a little ammonia by the decomposition of zinc cyanide before or during the experiment.

With sodium hydroxide and zinc cyanide the general effects observed were precisely similar to those just described, but rather less of the zinc cyanide was dissolved in the cold than would correspond to a reaction exactly parallel to that with potassium hydroxide. On heating the solution, however, a little more zinc oxide separated, and the proportion of zinc and cyanogen in solution then agreed closely with the formula  $\text{Na}_2\text{ZnCy}_4$ .

The solution of so large a proportion of zinc cyanide by the caustic alkalis (1 molecule for each molecule of hydroxide), when first brought together, is somewhat difficult of explanation. It seems most probable that some compounds, richer in zinc than the salts  $\text{Na}_2\text{ZnCy}_4$  and  $\text{Na}_2\text{ZnO}_2$ , are temporarily formed, *e. g.*, by some such reaction as the following,



which, being unstable in dilute solution, soon break up;



similar reactions taking place with the potassium compounds.

Although the potassium zinc cyanide,  $\text{K}_2\text{ZnCy}_4$ , is exceedingly stable at very varying temperatures and degrees of dilution, and crystallizes readily out of impure and strongly alkaline solutions, still the reaction



or a similar one, appears to take place, probably to a limited ex-

tent, when the double cyanide is mixed with potassium hydroxide in solution, for the gold-dissolving power of a double cyanide solution is considerably increased by addition of caustic alkali, the increment of solvent power decreasing for successive equal additions of alkali.

Several other reactions have been suggested as taking place between some of the substances investigated, but no experimental verification has been found for those investigated; for instance, the equation  $K_2ZnCy_4 + 2KOH = Zn(OH)_2 + 4KCy$  is contrary to all observed facts.

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### THE ALKALOIDS OF ADLUMIA CIRRHOSA.

BY J. O. SCHLOTTERBECK AND H. C. WATKINS.

Received March 31, 1903.

[SECOND PAPER.]

IN a previous paper,<sup>1</sup> "Adlunia Cirrhosa, a New Protopine-bearing Plant," the preliminary experiments upon the root of the first year's plant of this biennial were reported. Of the dried root only about 100 grams were available and it was treated as follows: It was first moistened with dilute ammonia water for the purpose of liberating the alkaloids from their combinations with acids. To avoid any possible change in the nature of the constituents, the powder was dried at room temperature by spreading out in thin layers in a room in which there was good circulation of air. The drug was now exhausted with chloroform in a Soxhlet apparatus since most free alkaloids are easily soluble in this solvent. The chloroform was recovered from the solution by distillation and the stiff, waxy residue then repeatedly digested with hot, very dilute acetic acid until all alkaloidal matter had been extracted. The combined acid aqueous extracts were concentrated, cooled, filtered and precipitated with ammonia water, being careful to avoid a great excess. The curdy precipitate was thoroughly washed on a filter, redissolved in dilute acetic acid, placed in a separator, made alkaline with ammonia and shaken out with ether. Solution of the alkaloid was almost instantaneous but only temporary. The ethereal liquid was passed through a tuft of cotton into a wide-mouthed flask and set aside. In a very short time

<sup>1</sup> *Am. Chem. J.*, 24, 249.



crystals began to separate and in the course of two hours most of the alkaloid had crystallized out. This alkaloid upon purification was found to be protopine, and at the time it was thought that this was the only alkaloid present in the root.

Wishing to continue the chemical study of this interesting and widely known plant, an endeavor was made to secure it in large quantities. Although it is claimed that it grows wild in wet woods from New England to Michigan and eastern Kansas southward, it was impossible to obtain the plant from botanic druggists, and collectors could not be found to gather it. It was then decided to grow it ourselves. The small, shiny black seeds were obtained without difficulty from seedsmen and sowed as directed, in spring. Not a single seed germinated that year. Not desiring to postpone the work for a year, growing plants were solicited from the citizens of Ann Arbor who grow it quite generally about porches and doorsteps. About 150 of the first year's plants and sufficient of the second year's vine to make about 15 pounds when dry were kindly donated. The growing plants were transplanted to the experimental garden and the following year's crop reserved for further study. It has since been learned that the seeds are very slow in germinating and must be sown in a cool, moist soil.

Self-sown seeds do not germinate as a rule until June of the following year.

In the present study the entire plant of the second year's growth was employed, no attempt being made to separate root from stem or leaves. The finely ground drug was treated exactly as outlined above. About 30 grams of a dirty gray mass of alkaloids was obtained and after redissolving in dilute acetic acid, making alkaline with ammonia water and shaking out with ether, several different forms of crystals separated. They were isolated as far as possible mechanically, and each one purified by many recrystallizations. Five distinct alkaloids were isolated by fractional crystallization as follows:

#### ALKALOID I, PROTOPINE.

The identity of this alkaloid was established in the preliminary examination which has been reported. It has the composition  $C_{20}H_{18}NO_6$  and melts at  $204^{\circ}$ - $205^{\circ}$  C.

ALKALOID II,  $\beta$ -HOMOCHELIDONINE.

This alkaloid crystallized in rather characteristic form, *vis.*, in beautiful clusters or rosettes of boat-shaped crystals with truncated ends. When purified, the crystals melted at  $159^{\circ}\text{C}$ . Sulphuric acid gives at once a rose-pink color which is intensified when the vapor of nitric acid is blown over it. Erdman's reagent colors it yellowish, then passing into beautiful violet.

Combustions gave the following results:

	Calculated for $\text{C}_{21}\text{H}_{29}\text{NO}_4$	Found.	
		I.	II.
Carbon.....	68.27	68.66	68.6
Hydrogen.....	6.24	6.2	6.9
Nitrogen.....	3.8	3.8	3.76

## ALKALOID III, ADLUMINE.

This alkaloid constituted the principal portion of the entire or total alkaloid. After purification it melted at  $188^{\circ}\text{C}$ . It crystallizes easily and in beautiful large crystals. A mixture of chloroform and alcohol constitutes the best crystallizing medium, from which large colorless, orthorhombic crystals can be obtained.

The following color tests were obtained:

Sulphuric acid.....	Lemon-yellow.
Erdmann's reagent .....	Olive-green to brown, then wine-red.
Nitric acid .....	Lemon-yellow to orange.
Marquis' reagent .....	Light yellow, changing to lavender.

A weighed quantity of desiccator-dried material lost no weight upon heating for several hours at  $100^{\circ}\text{C}$ . It therefore contains no water of crystallization. The material at hand permitted the following combustions for composition:

	Calculated for $\text{C}_{30}\text{H}_{39}\text{NO}_{12}$	Calculated for $\text{C}_{30}\text{H}_{41}\text{NO}_{12}$	Found.		
			I.	II.	III.
Carbon .....	65.62	65.45	65.95	65.77	65.45
Hydrogen ..	5.46	5.74	5.75	5.64	5.59
Nitrogen ...	1.97	1.96	2.08	2.18	2.02
Oxygen.....	26.95	26.85	26.22	26.41	26.94

From the above results alone it is impossible to determine, with certainty, whether the formula is  $\text{C}_{30}\text{H}_{39}\text{NO}_{12}$  or  $\text{C}_{30}\text{H}_{41}\text{NO}_{12}$ , the difference of two atoms of hydrogen being difficult to adjust because of the size of the molecule.

Platinum chloride does not precipitate the alkaloid from its solution. Gold chloride throws down a copious yellow, amorphous

precipitate, which can be crystallized by redissolving in hot water and allowing to cool. The crystals of the gold salt are deep orange-red in color, and contain no water of crystallization. During crystallization, a part of the gold is reduced. Incineration of the gold salt did not furnish concordant results, as we were probably dealing with a mixture of reduced gold and gold salt. This reaction will be studied further when more material is available.

*Determination of Methoxyls.*—Of the pure alkaloid, 0.100 gram was treated according to the Zeissel method for the determination of methoxyls. An abundant precipitate of AgI was formed in the flask containing the AgNO<sub>3</sub> solution. This was transferred to a Gooch crucible thoroughly washed, dried and weighed. The weight of AgI (0.847 gram) is equivalent to 8.68 per cent. methoxyl calculated from the formula having the higher hydrogen content. This is exactly equal to two methoxyl groups.

*Determination of Hydroxyls.*—A small amount of the pure alkaloid was heated with acetic anhydride on the steam-bath for several hours and the solution then evaporated to dryness. The amber-colored residue was taken up with a little chloroform, alcohol added and set aside. Colorless crystals, which melted at 177° C. when purified, separated quite rapidly.

Of this compound, 0.1412 gram was saponified by boiling with freshly prepared Mg(OH)<sub>2</sub> under a reflux condenser for two hours. Upon cooling, the liquid was filtered, the precipitate thoroughly washed, all the washings combined and concentrated and the magnesia determined as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The weight obtained was 0.0202 Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, which is equivalent to 5.54 per cent. of the acetic radical. Theory requires 5.68 per cent. for one acetyl group based on the formula with higher molecular weight.

The compound is then written C<sub>17</sub>H<sub>24</sub>(OH)(OCH<sub>3</sub>)<sub>2</sub>NO<sub>2</sub>.

Finally, this alkaloid, which we have named adlumine because it seems not to have been known before, rotates the plane of polarized light ( $\alpha$ )<sub>D</sub> = +39.88.

#### ALKALOID IV, ADLUMIDINE.

This alkaloid crystallizes in small, almost colorless, square plates melting at 234° C. When perfectly pure it is colorless, but it is extremely difficult to remove the last traces of the yellow color which adheres to it. It appears to be also a new alkaloid and we have therefore named it adlumidine.

The quantity available was too small to permit of more than the following combustions:

	Calculated for $C_{30}H_{29}NO_9$	Found.		
		I.	II.	III.
Carbon .....	65.6	65.69	....	65.45
Hydrogen .....	5.3	5.6	5.1	5.2
Nitrogen .....	2.54	2.6	....	2.63
Oxygen .....	26.5	26.11	....	26.72

The color reactions are striking.

Sulphuric acid..... Bright red, changing to olive-brown, then pink.

Erdmann's reagent .... Brick-red, changing to shades of green, to brown.

Nitric acid ..... Orange to light yellow.

Marquis' reagent ..... Bright red to dark brown, then purple-violet.

#### ALKALOID V, UNNAMED.

This alkaloid was found in such small quantity that only the melting-point  $176^{\circ}$ - $177^{\circ}$  C. and the color reactions could be determined.

Sulphuric acid ..... Light yellow.

Erdmann's reagent..... Dirty olive, brown, wine-red.

Nitric acid..... Light yellow.

Marquis' reagent..... No color.

#### ORGANIC ACIDS.

The dregs left after removing the alkaloids with chloroform were percolated with boiling water and the percolate concentrated to a small volume. Upon cooling, a crystalline sediment accumulated in the bottom of the dish. This dark-colored deposit was collected on a Büchner filter and thoroughly washed with cold water. There was left a grayish granular mass of salts of ammonia and calcium. This mass was dissolved in hot water with the aid of a little acetic acid, and then precipitated with a solution of lead subacetate. This precipitate was collected and rapidly washed with cold water by the aid of suction, then suspended in water and decomposed with hydrogen sulphide, the lead sulphide removed by filtration and the filtrate evaporated to dryness. This was boiled with alcohol and filtered. From the filtrate, a white precipitate separated, on cooling, which was found to contain calcium. Calcium tartrate was suspected. It was dissolved in acetic acid and treated with ammoniacal silver nitrate solution from which it deposited silver in the form of a mirror upon boiling. The free acid was precipitated by calcium hydroxide in the cold (distinction from citric acid).

The residue left after treating with boiling alcohol was tested with ammoniacal silver nitrate solution but it did not precipitate silver and was not precipitated by calcium hydroxide in the cold, though it was precipitated on heating.

The free acid was crystallized later and the rhombic prisms of citric acid identified.

#### SUMMARY.

*Adlumia cirrhosa* contains at least five distinct alkaloids as follows:

- (1) Protopine,  $C_{20}H_{19}NO_3$ , melting-point  $204^{\circ}$ - $205^{\circ}$  C.
- (2)  $\beta$ -Homochelidonine,  $C_{21}H_{23}NO_3$ , melting-point  $159^{\circ}$  C.
- (3) Adlumine,  $C_{35}H_{39}NO_{12}$  or  $C_{35}H_{41}NO_{12}$ , melting-point  $187^{\circ}$ - $188^{\circ}$  C.
- (4) Adlumidine,  $C_{30}H_{29}NO_9$ , melting-point  $234^{\circ}$  C.
- (5) Unnamed, melting-point  $176^{\circ}$ - $177^{\circ}$  C.

Also tartaric and citric acids.

The investigation is being continued.

SCHOOL OF PHARMACY, UNIVERSITY OF MICHIGAN,  
ANN ARBOR, MICH.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 78].

### 3-NITROPHTHALYL CHLORIDE AND ITS ACTION WITH AMMONIA AND WITH AROMATIC AMINES.

BY VICTOR JOHN CHAMBERS.

Received April 6, 1903.

THE action of phosphorus pentachloride upon 3-nitrophthalic acid has been tried before, but the product isolated from the reaction mass has not been the acid chloride. Boroschek<sup>1</sup> obtained the anhydride of 3-nitrophthalic acid and also the anhydride of 3-chlorophthalic acid. Levi<sup>2</sup> obtained only the anhydride of 3-nitrophthalic acid.

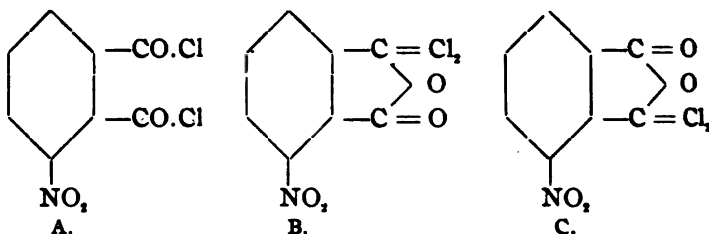
By using the process described in the experimental part, the author was able to obtain the acid chloride in the form of colorless, transparent, well-defined crystals melting at  $76^{\circ}$ - $77^{\circ}$  corr.

Phthalyl chloride, as is well known, has been assigned both a

<sup>1</sup> Inaug. Dissertation, 1901.

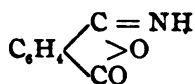
<sup>2</sup> Inaug. Dissertation, 1891.

symmetrical and an unsymmetrical structure. The presence of the nitro group in 3-nitrophthalyl chloride introduces another possibility. If the chloride be symmetrical it can have only the one structure, A, but if a asymmetrical it can have either of the two forms B and C.



The study of its action with various reagents, such as ammonia, substituted ammonias, alcohols and phenols, was undertaken in the hope of throwing some light upon this question. The action with ammonia and various substituted ammonias is reported in the present paper. The study of the action of alcohols and phenols is being carried on at the present time.

The action of ammonia upon phthalyl chloride has been tried under various conditions. Kuhara<sup>1</sup> passed dry ammonia gas over dry phthalyl chloride and obtained phthalimide as the result of a violent reaction. He also treated the chloride with aqueous ammonia and then the resulting solution with hydrochloric acid. On washing and crystallizing the product from alcohol, beautiful crystals were obtained that gave the same analytical results as phthalimide and yet showed different properties. He proposed the unsymmetrical structure



for the substance.

Auger<sup>2</sup> obtained a product he called the unsymmetrical amide of phthalic acid by treating the chloride with an excess of concentrated ammonia and evaporating over sulphuric acid. This amide, when treated with hydrochloric acid, gave a body isomeric with phthalimide.

Hoogewerff and Van Dorp<sup>3</sup> treated phthalyl chloride with a

<sup>1</sup> *Am. Chem. J.* 3, 26.

<sup>2</sup> *Ann. chim. phys.*, (6), 22, 289.

<sup>3</sup> *Rec. trav. chim. Pays-Bas*, 11, 84.

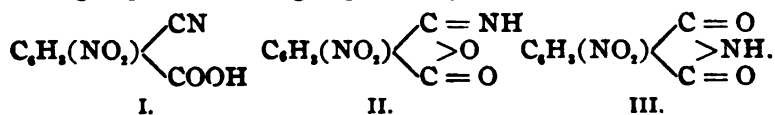
cold aqueous solution of ammonia, care being taken to prevent rise of temperature. After an excess had been added, the solution was acidified with hydrochloric acid. A crystalline substance separated that had the following properties: It melted at  $180^{\circ}$ - $190^{\circ}$ , solidifying again as the temperature rose and remelting at that of the imide; it had acid properties, forming a number of salts; it was easily decomposed by boiling with water and was changed to phthalamic acid by the action of concentrated sulphuric acid; it formed esters, and the ethyl ester was identical with that prepared by Miller from the *o*-cyanbenzoic acid made from anthranilic acid by the Sandmeyer reaction. The preparation of this acid from phthalyl chloride indicates the unsymmetrical structure for that chloride.

The action of dry ammonia upon dry 3-nitrophthalyl chloride was analogous to that upon the unsubstituted chloride. The imide was obtained.

The action of aqueous ammonia was different, however. No cyan acid could be obtained, the original 3-nitrophthalic acid being the only product. The reason for this was clear when it was found that the cyan acid, which was obtained by another method, was unstable in the presence of the slightest amount of water, passing to an acid ammonium salt of 3-nitrophthalic acid. This in turn gave the original nitrophthalic acid when acidulated. The action of aqueous ammonia upon a chloroform solution of the chloride, with cooling, was found to give a 3-nitrophthalamic acid.

The action of dry gaseous ammonia upon a dry ethereal solution of the chloride at a low temperature and subsequent treatment with hydrochloric acid gas gave a substance that had the same composition as 3-nitrophthalimide. This new substance melted at  $99^{\circ}$ - $100^{\circ}$  and then rearranged to the imide as the temperature was raised to  $105^{\circ}$ .

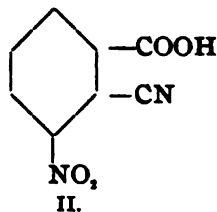
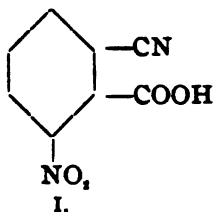
There are three possible structures that may be assigned to this body, leaving out of question for the moment the relation of the nitro group to the other groups. They are



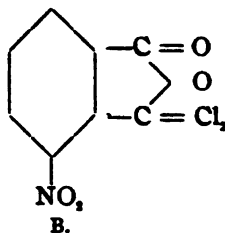
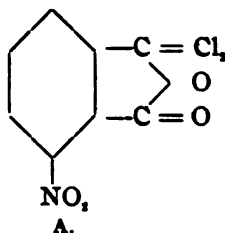
III is usually assigned to the well-known imide. Moreover, if ammonia gave, under the conditions described, a product to be

represented by either II or III it would be reasonable to expect that primary amines would give analogous bodies under like conditions. No such bodies could be obtained. It seems probable, therefore, that the substance in question is a nitrocyanbenzoic acid. One reason that Hoogewerff and Van Dorp gave for the cyan structure of the body they obtained by the action of ammonia upon phthalyl chloride was that the same body was formed by the introduction of CN in place of  $\text{NH}_2$  in anthranilic acid. This proof could not be applied in this case as the compound is unstable in the presence of water. In that respect it differs from *o*-cyanbenzoic acid. For the same reason it could not be changed to the corresponding amic acid by treatment with concentrated sulphuric acid and then with water.

There are, however, two possible formulas that may be assigned to a cyan acid derived from 3-nitrophthalyl chloride:



These would be derived from the two theoretically possible chlorides:

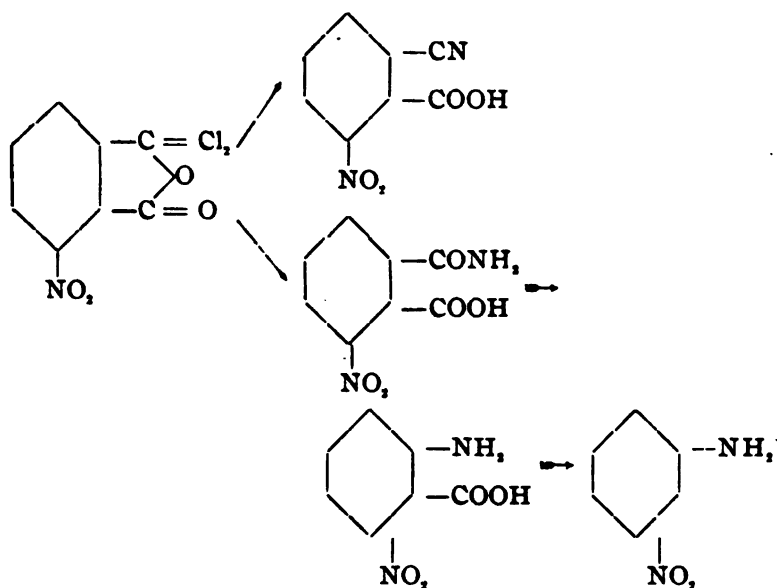


It was found that the cyan acid obtained is to be given formula I and that, in consequence, formula A is the correct one for 3-nitrophthalyl chloride, if that body is to be assigned an asymmetrical structure.

While 3-nitrophthalyl chloride gave a nitrocyanbenzoic acid under certain conditions, it gave a nitrophthalamic acid under others. It is fair to assume that the CN group in one case and the  $\text{CONH}_2$  group in the other are in the same position in the



molecule. The structure of this amic acid was obtained by the same method used by Kahn<sup>1</sup> to prove the structure of an acid methyl ester of 3-nitrophthalic acid. The nitrophthalamic acid was changed to a nitroanthranilic acid and its melting-point was that of the 2-nitro-6-aminobenzoic acid obtained by Kahn. Carbon dioxide was then eliminated from this acid and *m*-nitraniline obtained.



Van der Meulen<sup>2</sup> obtained phthalanilide by the action of aniline upon the hydrochloride of isophthalanil.

Rogow<sup>3</sup> shortly afterwards obtained it by the action of aniline upon phthalyl chloride.

Kuhara and Fukui<sup>4</sup> tried the action of a cold ethereal solution of aniline upon a similar solution of phthalyl chloride. A white solid was obtained which was washed with hydrochloric acid, ammonia, and water, and then extracted several times with small portions of boiling alcohol. It was crystallized from glacial acetic acid, and then from a large amount of boiling alcohol. A quantity of fine white needles was obtained. Analysis for nitrogen

<sup>1</sup> *Ber. d. chem. Ges.*, 35, 631.

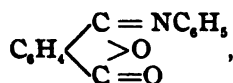
<sup>2</sup> *Rec. trav. chim. Pays-Bas*, 15, 323.

<sup>3</sup> *Ber. d. chem. Ges.*, 30, 1442.

<sup>4</sup> *Am. Chem. J.*, 26, 454.

indicated a composition similar to that of the phthalanil. It differed markedly, however, from the known phthalanil.

Kuhara and Fukui gave it the structure



asymmetrical phthalanil. A similar compound was obtained from phthalyl chloride and orthotoluidine.

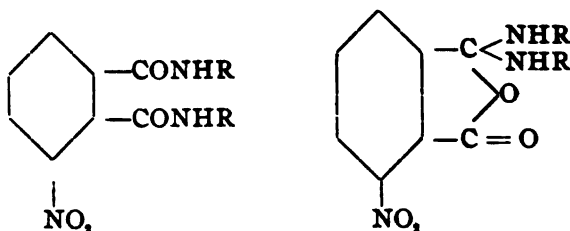
If a compound of this nature could be obtained when aniline is used instead of ammonia, it would point strongly to a similar structure for the so-called cyan acid.

The experiments of Kuhara and Fukui were tried with 3-nitrophthalyl chloride. A similar-looking product was obtained but analysis showed it to correspond to a 3-nitrophthalanilide. The experiment was tried a number of times with the same results. Paratoluidine, metanitroaniline and paranitraniline were substituted for aniline and similar products were obtained.

When the work was at this stage an article appeared by Hoogewerff and Van Dorp.<sup>1</sup> Their work indicated that Kuhara and Fukui really had phthalanilide which was transformed to phthalanil by the crystallization from glacial acetic acid.

That corresponded with the results obtained with 3-nitrophthalyl chloride and it only remained to show that the anilides obtained were also transformed to the anils by action of hot glacial acetic acid. This was found to be true in every case.

The action of a primary aromatic amine upon 3-nitrophthalyl chloride is then to introduce two molecules of the amine. The resulting compounds may have either of the two following structures:



No experimental proof was obtained that would indicate which of the two is the correct one.

<sup>1</sup> *Rec. trav. chim. Pays-Bas*, 21, 339.

## EXPERIMENTAL PART.

The chloride was made by the action of phosphorus pentachloride upon 3-nitrophthalic acid.

This acid was prepared by the Miller method as modified by Bogert and Boroschek.<sup>1</sup> 150 grams of phthalic anhydride were treated with a mixture of 225 grams of concentrated sulphuric acid and 225 grams of fuming nitric acid. The whole was heated in a roomy casserole on a water-bath until the nitrophthalic acids began to separate from the solution. About 20 cc. of water were then added and the whole heated a couple of hours longer. The mixture was then allowed to stand over night. The crystals were separated as completely as possible from the acid mother-liquor and dissolved in about 750 cc. of water. This solution was evaporated on a water-bath until a crust commenced to be formed. After standing quietly for from three to four hours, most of the 3-nitrophthalic acid separated as a hard crust on the walls of the container. A further small crop was obtained by evaporating the liquid again to two-thirds its bulk. The acid was purified by one recrystallization. Yield, about 50 grams.

Fifty grams of the acid in the state of a fine powder were mixed with 125 grams of phosphorus pentachloride and slowly heated in a casserole in a sulphuric acid bath. Action began at about 110°, the mass boiling violently. The heat was slowly raised to 140° or until the liquid began to develop a red color. On cooling, the reaction product became solid. This was reduced to a fine state of division and extracted with 400 cc. of carbon tetrachloride. After standing over night, most of the nitrophthalyl chloride separated as a mass of crystals somewhat red in color. To purify them they were powdered and crystallized twice from ligroin, boiling-point 60° to 80°. A fine white meal of crystals was obtained. Melting-point, 76°-77° (corr.).

The chloride separated as good-sized compact prisms when an ethereal solution was allowed to evaporate over sulphuric acid.

3-nitrophthalyl chloride is readily soluble in cold ether and chloroform and in warm carbon tetrachloride and ligroin. It is but little soluble in cold carbon tetrachloride or cold ligroin. It is quite stable when in the form of fair-sized compact crystals but is very unstable when in a fine state of division. The solvents used

<sup>1</sup> This Journal, 23, 740.

in its purification must be perfectly dry or there is a considerable loss due to the formation of the anhydride.

Analyses gave the following results:

	Theory for $C_6H_5(NO_2)(COCl)_2$	Found.	
		I.	II.
Carbon .....	38.74	39.00	....
Hydrogen .....	1.21	1.46	....
Nitrogen .....	5.66	5.91	....
Chlorine .....	28.55	28.53	28.26

#### ACTION OF AMMONIA.

*Dry Chloride and Dry Ammonia.*—A small quantity of the dry chloride was placed in a small flask and a current of dry ammonia passed over it. The reaction was violent, copious clouds of ammonium chloride being given off. The reaction mass became pasty and of a yellow color and very warm. The yellowish mass dissolved readily in a warm mixture of alcohol and acetone, giving small yellow crystals on standing. Melting-point,  $213^{\circ}$ - $215^{\circ}$ . Melting-point of 3-nitrophthalimide,  $215^{\circ}$ - $216^{\circ}$ .

*Chloroform Solution of the Chloride and Dilute Ammonia Water.*—A small quantity of the chloride was dissolved in about 75 cc. of chloroform. This was placed in a separatory funnel. Water and small pieces of ice were added and then successive small portions of dilute ammonia water until the odor of ammonia persisted after shaking and standing for ten minutes. The aqueous solution was separated from the chloroform and acidified with hydrochloric acid. Clusters of small, transparent plates separated on standing.

The melting-point of this substance was not constant. It melted to a clear liquid between  $150^{\circ}$  and  $157^{\circ}$ , according to rate of heating. A gas was given off at the same time that may have been confined air or a small amount of water coming from the decomposition of the substance. The substance solidified again at about  $160^{\circ}$  and remelted with vigorous evolution of water between  $200^{\circ}$  and  $205^{\circ}$ . When bubbling ceased, the product solidified again, if the temperature had not risen above  $210^{\circ}$  and remelted finally at  $214^{\circ}$ - $215^{\circ}$ , practically the melting-point of the imide. This behavior corresponds in part with that of 3-nitro-1-phthalamic acid.

To prove that it was such, it was transformed into 6-amino-2-

nitrobenzoic acid. The Hofmann method as used by Kahn<sup>1</sup> was followed. 2.1 grams of the amic acid were dissolved in 10 cc. of normal potassium hydroxide solution. The solution was well cooled and to it was added 0.5 cc. of bromine dissolved in 20 cc. of the normal alkali. The whole was well shaken and then treated with 30 cc. more of the alkali. On heating the yellow solution for an hour on a water-bath, its color changed to red. It was then placed in an ice-bath and carefully treated with 20.5 cc. of 2-N-hydrochloric acid, added drop by drop. The yellow mass that separated was crystallized from water. Beautiful leaves or sheaves of needle-like crystals were obtained melting with decomposition at 178°-180°. This corresponds with that of the 6-amino-2-nitrobenzoic acid obtained by Kahn. As a further proof, this body was changed to metanitriline. One gram was dissolved in 10 cc. of methyl alcohol, and 0.5 cc. of concentrated sulphuric acid was added and the whole heated in a flask connected with a return condenser for seven hours. The reaction product was poured into a small amount of water and neutralized with sodium carbonate. The yellow solid that separated was crystallized twice from hot water. Fine yellow needles were obtained that melted at 112°. The melting-point of metanitriline is 111°.

*Dry Ethereal Solution of the Chloride and Dry Ammonia.*—Two to three grams of the chloride were dissolved in 150 cc. of dry ether and placed in a freezing-mixture with a temperature of —5° to —10°. Dry ammonia gas was then passed in, whereupon the solution became milky. After the action was over, a stream of dry hydrochloric acid gas was passed through the mixture until it was no longer absorbed. The whole was filtered with suction. The clear, ethereal solution was diluted with 50 cc. of carbon tetrachloride and allowed to evaporate at room temperature in a current of dry air. Clusters of fine white needles were obtained. Nothing was found in the ethereal solution when the treatment with hydrochloric acid was omitted.

A small portion of this substance was placed in a melting-point tube and heated slowly. It melted to a clear liquid at 99°-100° and solidified again without apparent loss before the temperature reached 105°. It melted again without evolution of gas at 214°-215°.

<sup>1</sup> *Ber. d. chem. Ges.*, 38, 631.

To show that the cyan acid rearranged to the imide without loss, a weighed portion of it was placed in a platinum crucible and heated in an air-bath for thirty minutes to a temperature of  $125^{\circ}$ . The rearrangement described above took place but the change in weight was less than a milligram. The fused mass was dissolved in a warm mixture of alcohol and acetone and gave crystals of the imide.

A small amount of the cyan acid was dissolved in dry ether, and ammonia gas passed through the solution. A white, amorphous mass was obtained and the ethereal solution left no residue. This body was thought to be the ammonium salt. It lost ammonia and passed to the imide when heated above  $200^{\circ}$ . No other salts could be formed, as the cyan acid is so unstable in the presence of water.

Hoogewerff and Van Dorp obtained phthalamic acid by the action of concentrated sulphuric acid upon *o*-cyanbenzoic acid. The same experiment was tried with the nitrocyanbenzoic acid but the results were not the same. 3-nitrophthalic acid was the only result.

*Action of Water on the Cyan Acid.*—Two grams of the acid were dissolved in 25 cc. of warm water. On cooling, thin plates separated. They melted at  $140^{\circ}$  to  $145^{\circ}$  with no evolution of water, solidified again and then remelted with evolution of water at  $204^{\circ}$ - $205^{\circ}$ . The crystals were redissolved in a little water and kept warm,  $60^{\circ}$ - $65^{\circ}$ , for an hour. The crystals then obtained showed no sign of rearrangement but melted with evolution of water at  $208^{\circ}$ - $212^{\circ}$ . After all water had been driven off, the tube was allowed to cool. The contents were found to be the imide. The acid ammonium salt of 3-nitrophthalic acid was made and compared with the above. They were found to be identical.

Analysis of the nitrocyanbenzoic acid:

	Theory for $C_6H_5(NO_2)CN.COOH.$	Found.
Carbon .....	50.00	50.16
Hydrogen .....	2.08	2.10

#### ACTION OF PRIMARY AROMATIC AMINES UPON 3-NITROPHTHALYL CHLORIDE.

*Action of Aniline.*—A few grams of the nitrophthalyl chloride were dissolved in dry ether and cooled to  $-8^{\circ}$ . A cold solution of aniline was added very slowly, care being taken to keep the temperature from rising above  $-5^{\circ}$ . A pale yellow solid sepa-

rated at once. This was filtered off and washed with dilute hydrochloric acid and then with warm water. The white caseous residue was crystallized repeatedly from large amounts of boiling alcohol. The product separated in the form of white, fine needles that felted when filtered. Melting-point,  $211^{\circ}$ - $212^{\circ}$ , with decomposition. Analysis, as given below, showed the compound to be 3-nitrophthalanilide. It was insoluble in water, nearly so in cold alcohol, easily soluble in hot alcohol or glacial acetic acid. Prolonged boiling with water had no effect. Dilute sodium carbonate or hydroxide solution had no effect in the cold but liberated aniline when heated.

A small portion was heated for an hour to gentle boiling with glacial acetic acid. On cooling and diluting, crystals separated melting at  $135^{\circ}$ . Melting-point of 3-nitrophthalanil,  $134^{\circ}$ .

	Theory for $C_8H_5(NO_2)C_2O_2(NHC_6H_5)_2$	Found.
Carbon .....	66.48	66.45
Hydrogen .....	4.16	4.34
Nitrogen .....	11.63	11.82

*Action of Paratoluidine.*—The results obtained by using paratoluidine instead of aniline were perfectly analogous to those described above. The reaction was carried on in a similar manner, the result being a mass of fine, white needles that could not be told from those obtained from aniline. Melting-point,  $223^{\circ}$ - $225^{\circ}$ , with decomposition. Analysis showed the compound to be 3-nitrophthal-*p*-toluide.

When heated with glacial acetic acid for a short time it was changed to 3-nitrophthal-*p*-tolil, melting-point,  $152^{\circ}$ - $153^{\circ}$ .

Analysis of 3-nitrophthal-*p*-toluide.

	Theory for $C_8H_5(NO_2)C_2O_2(NHC_6H_4CH_3)_2$	Found.
Nitrogen .....	10.8	11.0

*Action of Metanitriline.*—The experiment was carried on in the same way as with aniline. The reaction was not as rapid.

The reaction-product was finally crystallized from a large amount of alcohol, giving a mass of small, white needles. They melted very poorly at  $225^{\circ}$  to  $230^{\circ}$ , with decomposition. Heating for two hours with glacial acetic acid dissolved them but also changed the substance to 3-nitrophthal-*m*-nitranil. Melting-point,  $218^{\circ}$ - $219^{\circ}$ .

Analysis of 3-nitrophthal-*m*-nitranilide.

	Theory for $C_6H_5(NO_2)C_7O_2(NHC_6H_4NO_2)_2$	Found.
Carbon .....	53.21	53.19
Hydrogen.....	2.88	2.78

*Action of Paranitraniline.*—The experiment was carried out in the usual manner. No solid separated from the cold ethereal solution but did when it was allowed to warm to the room temperature. This was purified by the usual process of washing and crystallizing from warm alcohol. Small, warty masses separated. Further crystallization from alcohol gave small, pale yellow needles melting with decomposition at 197°–200°. It was probably a product analogous to those described above. No analysis was made.

Treatment with glacial acetic acid gave fine, yellow needles melting at 248° to 249° with slight decomposition.

The melting-point of 3-nitrophthal-*p*-nitranil obtained by Bogert and Boroschek was 249°.

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## THE ACTION OF THE SODIUM SALTS OF DIBASIC ACIDS ON ANILINE HYDROCHLORIDE, AND OF ANILINE ON PHTHALYL CHLORIDE AND SUC- CINYL CHLORIDE.

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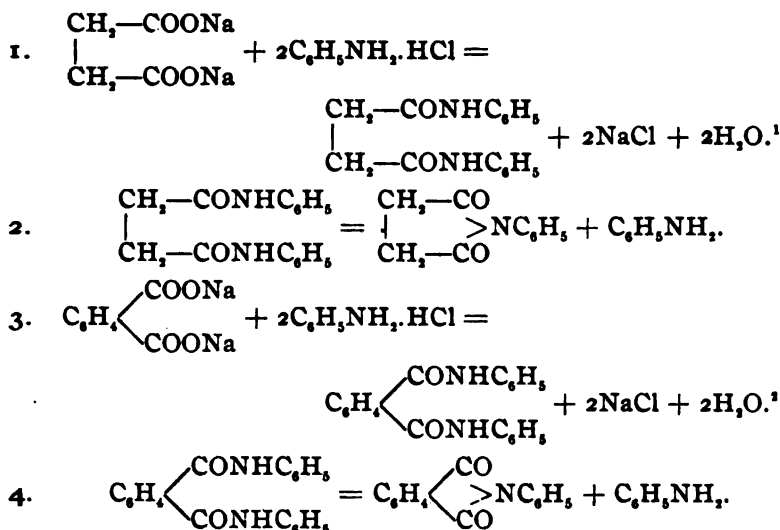
In this Journal,<sup>1</sup> the results of the action of the sodium salts of monobasic acids on the hydrochloride of aniline and of other amines, were reported by one of us. This study has been further extended so as to include the sodium salts of dibasic acids, sodium phthalate and sodium succinate being selected for this experimental work.

When dry sodium phthalate and aniline hydrochloride are heated together, phthalanil is formed, while sodium succinate and aniline hydrochloride produce succinanilide and succinanil. Phthalanil and succinanil are not formed directly from the sodium phthalate or the sodium succinate and the aniline hydrochloride, but they are only the final products, phthalanilide and succinanilide being first formed, then undergoing, at the high temper-

<sup>1</sup> This Journal, 24, 758 (1902).



ature at which the reaction is carried out, decomposition into aniline and the corresponding "anil."



In the products of the reaction between the sodium succinate and the aniline hydrochloride, both succinanilide and succinilide were isolated. The higher the temperature, the less the yield of succinanilide obtained. Phthalanilide, at its melting-point, passes readily into phthalanil, with the evolution of aniline vapors. In the case of the sodium phthalate and the aniline hydrochloride, no phthalanilide was isolated, phthalanil alone being obtained. Judging from analogy with the results obtained with the sodium succinate, phthalanilide must be first formed, then undergoing complete decomposition into phthalanil and aniline at a much lower temperature than that necessary for the complete conversion of succinanilide into succinilide and aniline; for at a temperature as low as  $130^\circ$ , the decomposition of phthalanilide is complete, provided this temperature is maintained for a sufficiently long time.

It should be noted that Verley<sup>2</sup> obtained succinimide by distilling a mixture of ammonium chloride and potassium succinate, the succinimide doubtless being produced by the potassium succinate

<sup>1</sup> It is quite likely that the sodium succinate and the sodium phthalate first form phenylammonium salts, as  $\begin{array}{c} \text{CH}_3\text{---COONH}_2\text{C}_6\text{H}_5 \\ | \\ \text{CH}_2\text{---COONH}_2\text{C}_6\text{H}_5 \end{array}$  and  $\text{C}_6\text{H}_4 \begin{array}{c} \text{COONH}_2\text{C}_6\text{H}_5 \\ \diagup \quad \diagdown \\ \text{COONH}_2\text{C}_6\text{H}_5 \end{array}$ , which, through loss of water, give respectively the phenylamides or anilides, as shown in equations 1 and 3.

<sup>2</sup> *Bull. Soc. Chim.*, [3], 9, 692 (1893).

first forming ammonium succinate, then succinamide, and finally succinimide. At about  $200^{\circ}$ , succinamide decomposes into succinimide and ammonia.

So far as we have been able to ascertain, phthalanilide was first prepared by van der Meulen,<sup>1</sup> who obtained it by boiling an aqueous solution of the hydrochloride of the iso-methyl ester of phenylphthalamic acid. He found that phthalanilide melted at  $251^{\circ}$ - $252^{\circ}$  with decomposition. The year following the appearance of van der Meulen's work, Rogow<sup>2</sup> made a further study of phthalanilide. Rogow states in his paper that phthalanilide had not previously been prepared; but he evidently overlooked the results obtained by van der Meulen. Rogow prepared phthalanilide by the interaction of phthalyl chloride and aniline. He used, as he says, not only a sufficient quantity of aniline to form this compound, but also enough more to combine with the free hydrochloric acid evolved. Rogow used 15 grams of aniline and 5 grams of phthalyl chloride, in which the aniline is in large excess. In this reaction, Rogow used alcohol as a diluent for the aniline, and to this solution, well cooled by salt and ice, the phthalyl chloride was added. The product of this reaction, phthalanilide, he found to have a melting-point of  $231^{\circ}$ , at which temperature it underwent decomposition. This decomposition, as has been mentioned, is due to the splitting up of this compound into aniline and phthalanil.

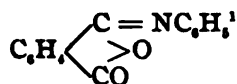
In 1901, Kuhara and Fukui<sup>3</sup> reported the results of their study of the action of aromatic amines on phthalyl chloride, at different temperatures. Among the various experiments which they carried out, was one on the action of aniline at ordinary temperatures. This reaction was brought about by allowing phthalyl chloride and aniline, both diluted with ether, to react on one another in the molecular ratio of 1:3 respectively. The only product they mention having obtained, is phthalanil. When, however, this same reaction was carried out at  $-10^{\circ}$ , the product obtained melted at  $218^{\circ}$ . and, upon analysis, gave results agreeing quite well for phthalanil. Phthalanil melts at  $203^{\circ}$ ; and as the product obtained at the low temperature was capable of being converted into the compound with a melting-point of  $203^{\circ}$  by heating in a sealed

<sup>1</sup> *Rec. trav. chim. Pays-Bas*, 18, 345 (1896).

<sup>2</sup> *Ber. d. chem. Ges.*, 30, 1442 (1897).

<sup>3</sup> *Am. Chem. J.*, 26, 454 (1901).

tube to  $140^{\circ}$  with *o*-xylol, they called their new product  $\alpha$ -phenylphthalimide, and assigned it the following structure:



Kuhara and Fukui do not mention Rogow's work, whose results are at direct variance with theirs. Moreover, their methods are practically identical, except that Kuhara and Fukui used ether as a diluent while Rogow dissolved the aniline in alcohol. Kuhara and Fukui also fail to mention the work of van der Meulen,<sup>2</sup> who describes, under the name of phthalphenylisoimide, a compound having the same structure as their  $\alpha$ -phenylphthalimide; but whose melting-point is  $115^{\circ}$ - $117^{\circ}$ .

This question of the products formed from the interaction of phthalyl chloride and aniline, we have resubmitted to experiment. The conditions under which we worked were identical with those of Kuhara and Fukui; namely, with ether as a diluent, at ordinary temperatures and at  $-10^{\circ}$ , as well as with the same reacting masses.

Three products are formed when the reaction is carried on at ordinary temperatures: aniline hydrochloride, phthalanilide, and phthalanil. So far as the phthalanilide is concerned, our results are the same as Rogow's; relative to the phthalanil, our results coincide with those of Kuhara and Fukui. Rogow, however, mentions no product other than phthalanilide, while Kuhara and Fukui mention phthalanil alone. From this we judge that, even if other products were formed, the ones mentioned were the principal products formed.

When ether solutions of phthalyl chloride and aniline react at ordinary temperatures, a heavy white precipitate is formed, consisting of aniline hydrochloride and phthalanilide, while the ether filtrate from this precipitate contains practically no other product except phthalanil, and this in but very small amounts. From

<sup>1</sup> The experimental portion of this paper referring to the action of phthalyl chloride on aniline was done previous to the appearance of the work of Hoogewerff and Van Dorp (*Rec. trav. chim. Pays-Bas*, 31, 339 (1902)), excepting the repetition of Kuhara and Fukui's work at low temperatures. The latter was finished previous to the appearance of the review of Hoogewerff and Van Dorp's work in the *Centralblatt*, 1903, I, 156, from which a knowledge of their work was first obtained. We have retained this portion of our experimental work as substantiating the findings of Hoogewerff and Van Dorp relative to the non-formation of  $\alpha$ -phenylphthalimide from aniline and phthalyl chloride.

<sup>2</sup> *Rec. trav. chim. Pays-Bas*, 18, 286 (1896).

these results, it appears that phthalanilide is the main product of the reaction. This experiment has been repeated a number of times, carrying out Kuhara and Fukui's directions as carefully as possible, but always with the results given above.

In carrying out this reaction at low temperatures, Kuhara and Fukui's directions were rigorously adhered to; but we have been unable to substantiate their results so far as the formation of the  $\alpha$ -phenylphthalimide is concerned. Kuhara and Fukui treated the reaction product, after filtering off the ether, with water, hydrochloric acid, and ammonia. The residual product they extracted with boiling alcohol a number of times, to remove the phthalanil, after which the remaining product,  $\alpha$ -phenylphthalimide, was purified by recrystallization from glacial acetic acid or alcohol, preferably the latter.

The results we obtained show that whatever phthalanil is formed in this reaction, remains in the ether filtrate, and that it is to be found there in only small amounts, mixed with phthalanilide. After treating the main product of this reaction with water, hydrochloric acid, and ammonia, we extracted the residue with boiling alcohol. In all, nineteen extractions had to be made with boiling alcohol before all this residue dissolved. From each one of these alcoholic fractions nothing but phthalanilide separated on cooling, with no trace of any other compound corresponding to  $\alpha$ -phenylphthalimide, with a melting-point of  $218^{\circ}$ .

From the results we have given, it appears that the principal product formed from the interaction of phthalyl chloride and aniline is phthalanilide, while phthalanil occurs in but small amounts, the results being independent of the temperature. Aniline hydrochloride is likewise formed in considerable amounts under both conditions of temperature.

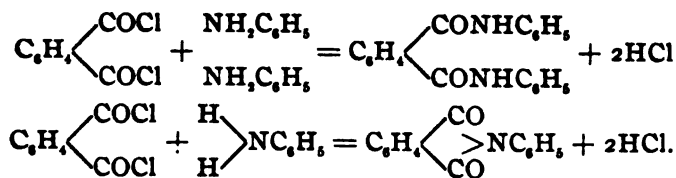
Phthalyl chloride, in a number of its reactions, deports itself as if it had an unsymmetrical structure. For example, with the Friedel and Crafts reaction, it yields diphenylphthalide;<sup>1</sup> on reduction with zinc and hydrochloric acid, phthalide is formed.<sup>2</sup> On the other hand, by reducing with glacial acetic and sodium amalgam, phthalyl chloride yields phthalyl alcohol,<sup>3</sup> a reaction very readily explained by the assumption of a symmetrical struc-

<sup>1</sup> *Ann. chim. phys.*, [6], 1, 523 (1884).

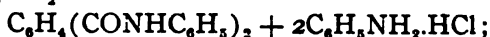
<sup>2</sup> *Ber. d. chem. Ges.*, 11, 237 (1878).

<sup>3</sup> *Ber. d. chem. Ges.*, 12, 646 (1879).

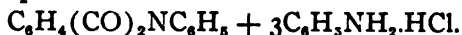
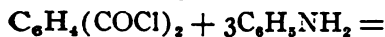
ture for phthalyl chloride. The formation of phthalanilide and phthalanil from phthalyl chloride and aniline, is readily explained by accepting in this case the symmetrical structure for phthalyl chloride.



Or, giving the complete equations, we have for the phthalanilide  $\text{C}_6\text{H}_4(\text{COCl})_2 + 4\text{C}_6\text{H}_5\text{NH}_2 =$



while for the phthalanil we have the following:



From these completed equations we can see that, in the first case, we have the phthalyl chloride and the aniline in the molecular ratio of 1:4, while in the second it is only 1:3. We have found in our experiments that, where these compounds were brought together in the ratio of 1:3, the ether filtrate always contained some unchanged phthalyl chloride.

The reaction between succinyl chloride and aniline was also studied, but only at ordinary temperatures. In this case, the products formed were succinanilide and aniline hydrochloride, but no succinanil was isolated. If succinanil is formed in this reaction, it is only in quite small amounts.

In the majority of its reactions, succinyl chloride acts as if it were  $\gamma$ -dichlorobutyrolactone. For example, it passes into butyrolactone on reduction;<sup>1</sup> it reacts with zinc ethyl to produce  $\gamma$ -diethylbutyrolactone;<sup>2</sup> with the Friedel and Crafts reaction it forms  $\gamma$ -diphenylbutyrolactone, but at the same time produces 10 per cent. of symmetrical dibenzoylthane.<sup>3</sup> The fact that symmetrical dibenzoylthane is formed, together with the  $\gamma$ -diphenylbutyrolactone, shows that succinyl chloride deports itself in this reaction like a mixture of the symmetrical and unsymmetrical forms, the latter being predominant. Inasmuch as succinanilide is the sole

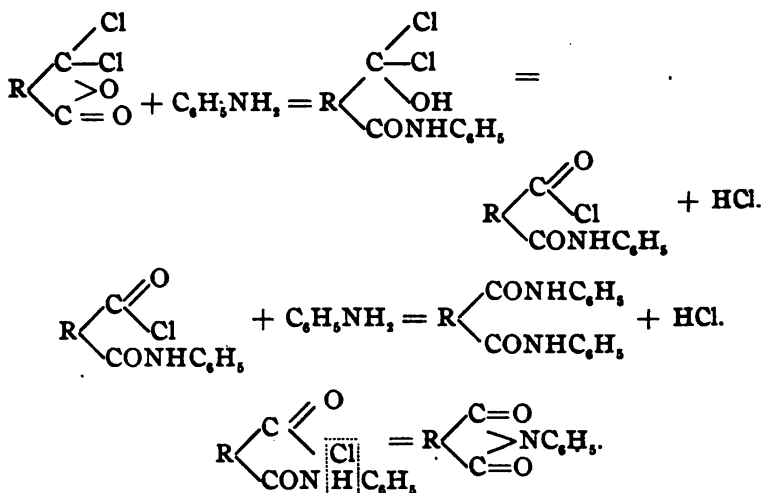
<sup>1</sup> *Ann. Chem.* (Liebig), 171, 261 (1874); *J. prakt. Chem.*, [2], 28, 63 (1882).

<sup>2</sup> *Ber. d. chem. Ges.*, 18, 1851 (1882).

<sup>3</sup> *Ann. chim. phys.*, [6], 22, 312 (1891).

product of the interaction of succinyl chloride and aniline, we can consider that in this case, as with the phthalyl chloride, the succinyl chloride has a symmetrical structure. These reactions with phthalyl chloride, succinyl chloride, and aniline, can not, however, lead us to any definite conclusions regarding the constitution of these acid chlorides, for the products formed may be explained from a standpoint of an unsymmetrical structure.

For example:



So far as we can see, there is no reason for believing that either phthalanilide or succinanilide have other than the symmetrical structure.

#### EXPERIMENTAL PART.

##### ACTION OF SODIUM PHTHALATE ON ANILINE HYDROCHLORIDE.

Dry sodium phthalate and aniline hydrochloride were ground up together in the proportion of one molecular weight of the former to two of the latter. The ground mixture, which developed the odor of aniline quite strongly, was heated in a sealed tube for six hours at 200°. There was no pressure on opening the tube. The solid contents of the tube were ground up several times with water, the water being decanted through a filter. The residue was treated in the same manner with dilute hydrochloric acid, and then given a final washing with water. The product thus obtained was

grayish in color. After several washings with small quantities of cold alcohol, the residue was recrystallized from boiling alcohol. The product thus obtained melted at  $203^{\circ}$ . The melting-point, crystalline form, and solubility in various solvents, were sufficient to identify this product as phthalanil. No phthalanilide was isolated from the products of this reaction; that is, at a temperature considerably below what must be the true melting-point of the phthalanil, this body breaks down into phthalanil and aniline, provided the heating be sufficiently prolonged.<sup>1</sup> From the product obtained by heating sodium phthalate and aniline hydrochloride to only  $132^{\circ}$  for five hours, no phthalanilide was isolated.

#### ACTION OF SODIUM SUCCINATE ON ANILINE HYDROCHLORIDE.

Sodium succinate and aniline hydrochloride in the molecular ratio of 1:2 respectively, were ground together and this mixture heated as in the case of the former experiment. The temperature during the heating reached  $360^{\circ}$ ; and while the resulting mass was very dark-colored, both succinanilide and succinanil were obtained from it. A repetition of this experiment, where the heating of the sealed tube was carried on for four hours, and the maximum temperature reached was but  $245^{\circ}$ , gave a product much lighter in color than in the previous experiment, and yielded the same reaction products. There was a considerable amount of free aniline formed. The contents of this second tube, after washing with cold water and dilute hydrochloric acid, was extracted with boiling water. On cooling, this aqueous extract separated a large amount of slightly colored crystals. Recrystallization from hot water and treatment with bone-black gave a perfectly white product which crystallized in long needle-like crystals, having a melting-point of  $150^{\circ}$ .

The portion of the original product that was insoluble in water, was dissolved in boiling alcohol and treated with bone-black. This solution, on cooling, separated a crystalline product, which was further purified by several recrystallizations from alcohol. This product had a melting-point of  $226^{\circ}$ .

The compound with a melting-point of  $150^{\circ}$  gave 8.29 per cent. N. Calculated for  $C_{10}H_9O_2N$ , 8 per cent.

The product soluble in water was thus identified by its melting-

<sup>1</sup> For a discussion of the melting-point of phthalanilide, see the experimental portion of this paper on the action of phthalyl chloride on aniline.

point, and by analysis, as succinanil, while the substance obtained from the alcohol, which had a melting-point of  $226^{\circ}$ , proved to be succinanilide, and on analysis gave 10.7 per cent. N. Calculated for  $C_{10}H_{10}O_2N_2$ , 10.44 per cent.

In the experiment in which the mixture of sodium succinate and aniline hydrochloride were heated to  $245^{\circ}$ , 15 grams of the former substance and 24 grams of the latter were used. From the resulting product, 11.6 grams of succinanil and 3.3 grams of succinanilide were obtained. The higher the temperature at which this reaction is carried out, the larger the relative yield of succinanil.

#### ACTION OF PHTHALYL CHLORIDE ON ANILINE.

Freshly distilled phthalyl chloride and aniline (in the ratio of one molecular weight of the former to three of the latter) were each dissolved separately in about 300 cc. of ether which had been carefully dried over sodium wire. The aniline solution was slowly added, with constant stirring, to the ether solution of the phthalyl chloride, both solutions being at room temperatures. The reaction caused hardly any perceptible rise in temperature. The addition of the aniline solution produced a heavy white precipitate, which was filtered, washed with ether, and then dried. The ether filtrate, on standing over night, deposited crystals which were filtered off and purified by crystallization from alcohol. These crystals proved to be phthalanilide. The ether filtrate from these phthalanilide crystals, which had deposited on standing over night, was evaporated to dryness and the residue purified by crystallization from alcohol. This product had a melting-point of  $203^{\circ}$ , and analysis gave results showing that this product was phthalanil. The phthalanilide which separated from the ether solution, had no well-defined melting-point. According to the rapidity of heating, the melting-point could be varied from  $20^{\circ}$  to  $25^{\circ}$ , the product always melting with gas evolution (aniline). In its behavior in a melting-point tube, phthalanilide behaves very much like phthalic acid, of which substance no well-defined melting-point can be had, on account of the ease with which it breaks down into phthalic anhydride and water. If the temperature of  $225^{\circ}$  be held for some time, phthalanilide will finally melt with gas evolution; but, with the ordinary rapidity with which melting-points are taken, the melting-point of phthalanilide usually obtained by us lay some-



where between  $240^{\circ}$  and  $250^{\circ}$ , while occasionally the melting-point would run still higher. This variable melting-point is doubtless due to the production of more or less phthalanil (m. p.  $203^{\circ}$ ) at a temperature below the true melting-point of the phthalanilide, which phthalanil, as soon as formed, lowers the melting-point of the whole mass.

The white precipitate obtained by the action of the aniline on the phthalyl chloride was, after drying, treated with hot water to remove the aniline hydrochloride. The residue was recrystallized from boiling alcohol, in which, however, it is not very soluble. The only product obtained was phthalanilide. Three analyses were made of this phthalanilide, the per cents. of nitrogen found being 9.11, 9.08, and 9.11, instead of 8.86 per cent. as calculated.

#### ACTION OF SUCCINYL CHLORIDE ON ANILINE.

In this experiment, freshly distilled succinyl chloride and aniline, both diluted with dry ether, were allowed to interact at ordinary temperatures. An excess of aniline a little greater than the molecular ratio of one of succinyl chloride to three of aniline, was found necessary in order to completely decompose the succinyl chloride. More heat seemed to be developed by this reaction than in the case where phthalyl chloride was used. In fact, if the ether solution of the aniline was added too fast to the ether solution of the succinyl chloride, sufficient heat was developed to cause the solution to boil. The heavy white precipitate produced, was filtered, washed with ether, and dried. Then after thoroughly washing with water, in order to free the product from aniline hydrochloride, the residue was purified by crystallization from alcohol. The pure product had a melting-point of  $226.5^{\circ}$ , and on analysis proved to be succinanilide. Found, 10.53 per cent. N. Calculated, 10.45 per cent.

The ether filtrate was evaporated to dryness, and an oily product, smelling strongly of aniline, was obtained, showing that an excess of aniline had been used in the reaction. This residue was, however, small in amount. On standing for some time *in vacuo* over sulphuric acid, this oily product became of a pasty consistency. No succinanil was obtained from this residue. If succinanil is formed by the interaction of succinyl chloride and aniline under the conditions we used, it is only in quite small amounts.

## SOME DERIVATIVES OF *p*-SULPHOCINNAMIC ACID.

BY F. J. MOORE.

Received April 15, 1903.

THE action of fuming sulphuric acid upon cinnamic acid was first thoroughly studied by Rudnew,<sup>1</sup> who isolated from the sulphonation mixture, two acids: one, the now well-known *p*-sulphocinnamic acid, which is the principal product of the reaction; and the other, an isomer which he called a meta-compound. Since that time the true *m*-sulphocinnamic acid has been prepared synthetically by Kafka,<sup>2</sup> and as its properties do not agree with those of the acid described by Rudnew, it is probable that the latter is an ortho-compound.

Rudnew's method of isolating these acids from the sulphonation mixture was the familiar one of treating the products of the reaction with barium hydroxide. The sulphonic acids were then separated from each other, and from the masses of barium sulphate produced, by crystallization from water. This method is tedious at best, and when one only wishes to prepare the para acid (as in the present investigation) it is better to take advantage of the fact (apparently heretofore overlooked) that this acid crystallizes spontaneously from the sulphonation mixture upon appropriate dilution with water. The *p*-sulphocinnamic acid used in this investigation was prepared in accordance with the following procedure. 150 grams of fuming sulphuric acid (containing 15 per cent. to 20 per cent. anhydride) are placed in a flask and 50 grams of finely ground cinnamic acid are introduced in small portions with constant shaking. The temperature rises during the reaction, and the quantities of cinnamic acid added are so regulated that the flask in which the sulphonation takes place shall not become uncomfortably warm to the hand. At the close, the reaction becomes sluggish, and may be concluded by heating for fifteen or twenty minutes on the water-bath. At this point the mixture should not be dark brown in color and should smell only faintly of sulphur dioxide. When cold, it is diluted with about three times its volume of water, and allowed to stand over night. If crystals of the *p*-sulphocinnamic acid are at hand, they should be added as soon as the diluted acid has become cold. Crystalliza-

<sup>1</sup> Rudnew: *Ann. Chem. (Liebig)*, 179, 8.

<sup>2</sup> Kafka: *Ber. d. chem. Ges.*, 34, 746.

tion then begins almost at once—usually at the bottom of the flask—but proceeds very slowly. It is seldom complete in less than ten hours, but at the end of that time the contents of the flask usually seem entirely solidified. It is usually best to determine the proper amount of dilution by experiment, with small portions, as different sulphonations, under apparently identical conditions, sometimes require slightly different treatment. The crystals thus obtained are filtered off and dried by suction. They are sufficiently pure for most purposes. A perfectly pure product is best obtained by dissolving the crude acid in water, precipitating the acid barium salt by means of a solution of barium chloride, purifying this by crystallization, and finally decomposing it with the calculated amount of sulphuric acid. On evaporation, the acid is obtained in the long four-sided prisms described by Rudnew. He describes these crystals as stable in the atmosphere,—an observation which I cannot confirm, possibly on account of the greater dryness of the American climate. The crystals which I obtained were very large and well formed, often showing beautiful twin-formation, but they weathered rapidly on exposure to the air. The acid was characterized by the preparation of the amide described by Palmer,<sup>1</sup> and by the crystalline form of the acid barium salt described by Rudnew, which crystallizes in beautiful long needles very difficultly soluble in cold water.

Previous investigators do not seem to have noticed the fact that this acid forms very insoluble acid salts with a number of the aromatic amines, and these salts offer a more convenient means of characterizing this acid than either of the methods mentioned above. Only the aniline salt was analyzed. This may be prepared by treating a solution of the acid, or any of its more soluble salts, with a solution of aniline hydrochloride. A crystalline precipitate appears at once, and on recrystallization from hot water, the salt shows a marked tendency to form large radially arranged aggregates. These crystals melt at 246° (uncorrected) and their composition is established by the following analysis.

Calculated for  $C_{13}H_{16}O_5NS$ : C, 56.08 per cent.; H, 4.67 per cent.; N, 4.35 per cent. Found: C, 56.07 per cent.; H, 4.82 per cent.; N, 4.77 per cent.

*Acid Sodium Salt.*—In the preparation of sulphocinnamic acid,

<sup>1</sup> Palmer: *Am. Chem. J.*, 4, 163.

as above described, a somewhat larger yield may be obtained by pouring the mother-liquor from the crystals of free acid into a saturated solution of sodium chloride. The acid sodium salt then separates out, and may be purified by crystallization from water. As this salt has not been heretofore described, the following analytical data are appended:

Calculated for  $C_9H_7O_5SNa \cdot 2H_2O$ : Na, 8.04 per cent.;  $H_2O$ , 12.59 per cent. Found: Na, 7.93 per cent.;  $H_2O$ , 12.59 per cent. at  $110^\circ$ .

*p*-Sulphodibromhydrocinnamic Acid.—*p*-Sulphocinnamic acid absorbs two equivalents of bromine with great readiness, even in aqueous solution. For this purpose, the acid is dissolved in just enough cold water to make a clear solution, and the calculated amount of bromine is added in portions of about a cubic centimeter with constant shaking. Any excess of bromine is finally removed by a current of air. A large part of the bromine addition product now separates as a fine, white, crystalline powder, and an almost quantitative yield may be obtained by evaporation of the mother-liquor in the cold. The first portions of the acid to be precipitated are very pure, but, for purposes of analysis, the acid was recrystallized from water, and then air-dried.

Calculated for  $C_9H_5Br_2S \cdot 2H_2O$ : C, 25.15 per cent.; H, 2.83 per cent.; Br, 37.20 per cent.; S, 7.54 per cent.;  $H_2O$ , 8.25 per cent. Found: C, 25.21, 25.22, 25.38 per cent.; H, 2.85, 3.00, 2.79 per cent.; Br, 37.15, 37.65, 37.32 per cent.; S, 7.93, 7.77, 7.59 per cent.;  $H_2O$ , 6.05, 7.73, 6.68 per cent.

One hundred parts of saturated solution at  $20^\circ$  contain from 53 to 57 parts of solid acid.

It is evident from the above, that the acid does not give up quite all its water of crystallization at  $110^\circ$ , but continued heating at a higher temperature results in slight decomposition as shown by a brown discoloration of the material.

*Barium Salt*.—The most characteristic inorganic salt of this acid is the acid barium salt, which is precipitated when a solution of the acid is treated with barium chloride. It crystallizes in short colorless needles.

Calculated for  $C_{18}H_{14}O_{10}S_2Br_4Ba_4 \cdot 4H_2O$ : C, 21.98 per cent.; H, 2.24 per cent.; S, 6.36 per cent.; Br, 32.55 per cent.; Ba, 13.94 per cent.;  $H_2O$ , 7.32 per cent.

Found: C, 21.64 per cent.; H, 2.40 per cent.; S, 6.64 per cent.; Br, 32.52 per cent.; Ba, 14.37 per cent.;  $H_2O$ , 8.10 and 7.34 per cent.

100 parts saturated solution contain 2.7 parts of solid salt.

*Copper Salt*.—When concentrated solutions of the acid are treated with a concentrated solution of copper sulphate, a white precipitate is obtained. This may be recrystallized from water, and then forms small wart-like aggregates of a pale greenish white color, which show some tendency to decompose when half dry, but which, when perfectly dry, are quite stable. The substance is evidently an acid salt.

Calculated for  $C_{18}H_{14}O_{10}Br_4S_2Cu_2 \cdot 2H_2O$ : Br, 36.63 per cent.; S, 7.32 per cent.; Cu, 7.28 per cent.;  $H_2O$ , 4.12 per cent.

Found: Br, 35.38, 35.10 per cent.; S, 7.25, 7.39 per cent.; Cu, 7.11, 7.43 per cent.;  $H_2O$ , 4.50 per cent. at  $110^\circ$ .

The results for bromine can hardly be considered satisfactory, but the salt is not well characterized, and another analysis did not seem worth while. It is very soluble in water.

*Sodium Salts*.—The acid sodium salt was prepared by the action of bromine upon the acid sodium salt of *p*-sulphocinnamic acid. It is a white crystalline powder.

Calculated for  $C_9H_7O_3BrSNa \cdot 3H_2O$ : Br, 34.48 per cent.; S, 6.90 per cent.; Na, 4.95 per cent.;  $H_2O$ , 11.63 per cent.

Found: Br, 34.76 per cent.; S, 7.30 per cent.; Na, 5.21 per cent.;  $H_2O$ , 11.69 per cent.

The neutral sodium salt was prepared by treating a solution of the free acid with sodium hydroxide until the solution was neutral to phenolphthalein. This salt crystallizes in needles very soluble in water.

Calculated for  $C_9H_6O_3Br_2SNa_2 \cdot 4H_2O$ :  $H_2O$ , 14.03 per cent. Found:  $H_2O$ , 14.02 per cent.

*Ammonium Salt*.—When a solution of the free acid is treated with an excess of ammonia and evaporated in a desiccator over sulphuric acid, crystals appear which probably consist of the neutral ammonium salt, but an analysis was impracticable, as the salt is not stable, and the products of decomposition have not yet been determined. They will be an object of subsequent study.

*Amide*.—*p*-Sulphocinnamic acid and its salts react vigorously

with phosphorus pentachloride. The acid chloride thus formed has not been isolated, but the reaction-mixture was poured into dilute ammonia with the object of preparing the amide. A product was thus formed which crystallizes from hot water (in which it is soluble only with difficulty) in bulky scales. These melt sharply at  $208^{\circ}$  (uncorrected) and decompose just above the melting-point with evolution of bromine. This substance is doubtless the diamide in which both hydroxyl groups of the acid are replaced by amido-groups, although the analytical results (especially for nitrogen) have never been entirely satisfactory. The yield is poor—never better than 10 per cent. of the material used. Other less well-characterized products sometimes appear, and the amide seems to undergo some decomposition in the treatment with hot water necessary for recrystallization.

Calculated for  $C_8H_{10}O_2N_2BrS$ : N, 7.25 per cent; Br, 41.45 per cent.; S, 8.29 per cent.

Found: N, 8.22 per cent.; Br, 41.18 per cent.; S, 8.44 per cent.

*Salts with Organic Bases.*—When the acid is treated with aniline hydrochloride in aqueous solution, a white crystalline precipitate is obtained. Salts of most of the aromatic amines seem to behave in a similar way. Among those tried were aniline, dimethyl aniline, diethyl aniline, quinoline,  $\alpha$ - and  $\beta$ -naphthyl amine, phenylene diamine, and diphenyl amine. It should be noted that neither pyridine nor any of the aliphatic amines yield similar precipitates, so far as tried. Most of the salts of the aromatic amines thus obtained crystallize well, and the aniline, dimethyl aniline, and diethyl aniline salts also melt sharply. They therefore furnish the most convenient method of characterizing the acid. The three salts just mentioned are all acid salts, as is shown by the analyses given below; the others probably have similar composition, but were not analyzed. All may be crystallized from hot water, the dimethyl aniline salt producing the best-formed crystals.

Aniline salt, white needles, melting-point  $192^{\circ}$ .

Calculated for  $C_{18}H_{15}O_2NBr_2S$ : Br, 33.27 per cent.; S, 6.65 per cent.; N, 2.91 per cent.

Found: Br, 33.52, 33.43 per cent.; S, 7.01, 6.82 per cent.; N, 3.05, 3.27 per cent.

One part of salt dissolves in 67 parts of water at room temperature.

Diethyl aniline salt, melting-point 160°.

Calculated for  $C_{19}H_{22}O_2NBr_2S$ : C, 42.45 per cent.; H, 4.28 per cent.; N, 2.61 per cent.; Br, 29.80 per cent.; S, 5.96 per cent.

Found: C, 42.25 per cent.; H, 4.19 per cent.; N, 2.80 per cent.; Br, 29.63, 29.89 per cent.; S, 6.14, 6.13 per cent.

Dimethyl aniline salt, clear prisms melting at 150°.

Calculated for  $C_{17}H_{18}O_2NBr_2S$ : C, 41.02 per cent.; H, 3.73 per cent.; N, 2.75 per cent.; Br, 31.44 per cent.; S, 6.29 per cent.

Found: C, 40.59 per cent.; H, 3.89 per cent.; N, 3.25 per cent.; Br, 31.09 per cent.; S, 6.31 per cent.

*Action of Silver Nitrate upon p-Sulphodibromhydrocinnamic Acid.*—When an aqueous solution of the free acid or its salts is treated with a solution of silver nitrate, a precipitate is formed. This is sometimes curdy, but when both solutions are concentrated, a separation of short needle-like crystals is sometimes observed. This may be a silver salt of the organic acid, but, if so, it is extremely unstable, and in a few minutes at longest, the precipitate consists entirely of silver bromide. In dilute solutions in the cold, it may be determined by a rough titration that precipitation ceases when one molecule of silver nitrate has been added to one of the acid. Salts of lead and mercurous mercury act in this respect like silver. The result, in any case, seems to be a splitting-off of one molecule of hydrobromic acid from the side-chain, resulting in the formation of a *p*-sulphobromcinnamic acid. This acid has not yet been isolated, and even the salts are difficult to obtain. When silver nitrate is used to remove the hydrobromic acid, the nitric acid set free by the reaction seems to have an oxidizing action upon the new product formed. The substitution of other salts for silver nitrate has hitherto involved somewhat similar difficulties. On one occasion, when the acid sodium salt of *p*-sulphodibromhydrocinnamic acid had been treated with dilute silver nitrate solution, the silver bromide produced filtered off, and the filtrate evaporated in a vacuum desiccator over sulphuric acid; crystals were obtained, for whose purity no guarantee could be given, but the analytical data presented below would seem to indicate the presence of an acid sodium salt of *p*-sulphomonobromcinnamic acid. Nothing conclusive is claimed for the results.

0.1996 gram substance yielded 0.1037 gram AgBr and 0.1352 gram BaSO<sub>4</sub>.

0.2654 gram substance lost 0.0085 gram at 135°.

Calculated for  $C_9H_7O_2BrSNa \cdot H_2O$ : Br, 23.05 per cent.; S, 9.22 per cent.;  $H_2O$ , 5.19 per cent.

Found: Br, 22.11 per cent.; S, 9.30 per cent.;  $H_2O$ , 3.54 per cent. at 135°.

*Action of Aqueous Hydrobromic Acid upon p-Sulphocinnamic Acid.*—The fact that sulphocinnamic acid adds bromine in aqueous solution, rendered it probable that hydrobromic acid might be added with equal readiness. Some of the acid was therefore dissolved in concentrated hydrobromic acid. It is only soluble with difficulty in this medium, and the acid was warmed to hasten solution. A few hours later, the flask was found to be traversed in all directions by thin, needle-like crystals, whose length seemed only limited by the dimensions of the flask. These crystals were filtered off, the mother-liquor removed as much as possible by suction, and the crystals air-dried. Washing with pure water was impracticable on account of their solubility in this medium. It was supposed at first that these crystals represented the hydrobromic acid addition product sought. A bromine determination, however, showed that the bromine content was small and variable, and evidently due only to contamination from the mother-liquor.

0.1567 gram substance yielded 0.0034 gram AgBr.

0.1763 gram substance yielded 0.0068 gram AgBr.

This is equivalent to 0.92 per cent. and 1.64 per cent. Br respectively.

The possibility remained that the crystals might be unchanged *p*-sulphocinnamic acid. This seemed at first very improbable as they are very different in appearance from the large four-sided prisms with oblique ends which this acid forms when crystallized from water. A further difference existed in the fact that while the latter weathered rapidly on exposure to the air, the new crystals were very stable in the atmosphere, and only lost water over sulphuric acid. This could be accounted for if the new crystals contained less water than the old. This proved to be the case. The analysis shows that the former contain 3 molecules of water of crystallization while the latter, as described by Rudnew, contains 5. The chemical identity of the two substances was shown by dissolving the new crystals in water and adding aniline hydro-



chloride. The acid aniline salt above described, melting at  $246^{\circ}$ , was precipitated.

Calculated for  $C_9H_8O_3 \cdot 3H_2O$ , 19.22 per cent.

Found:  $H_2O$ , 20.36 and 20.00 per cent at  $110^{\circ}$ .

The results are slightly high, but when it is remembered that these crystals contain some hydrobromic acid, which would also be lost at this temperature, they may be considered conclusive.

The above results are published on account of a temporary interruption of the work. It will, however, be again taken up, and I desire to reserve the field of the halogen derivatives of *p*-sulpho-cinnamic acid for some time longer.

My hearty thanks are due to my assistant, Mr. L. A. Salinger, who did most of the manipulative work, and conducted most of the analyses recorded in this paper.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
April 13, 1903.

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## THE ANALYTICAL CONSTANTS AND COMPOSITION OF MYRTLE WAX.

BY WARREN RUFUS SMITH AND FRANK BERTRAM WADE.

Received April 10, 1903.

MYRTLE wax, also known as laurel wax or bayberry tallow, is a fat of minor commercial importance obtained from the fruit of *myrica cerifera*, a shrub common along the North Atlantic sea-coast and in other sections of this country. The statements regarding its composition are somewhat contradictory. The general books of reference state that it is mainly free palmitic acid with about 20 per cent. palmitin. Some state that it also contains lauric acid and others that it contains stearic and myristic acids. The first of these statements is due to Moore,<sup>1</sup> the second to Chevreul.<sup>2</sup>

On the other hand, the works on oil and fat analysis state that myrtle wax is a triglyceride with a small amount of free fatty acid, and give low "acid values" in support of these statements. Benedict<sup>3</sup> states that it is composed mainly of palmitin with some myristin and stearin. Lewkowitsch<sup>4</sup> says that in addition to the

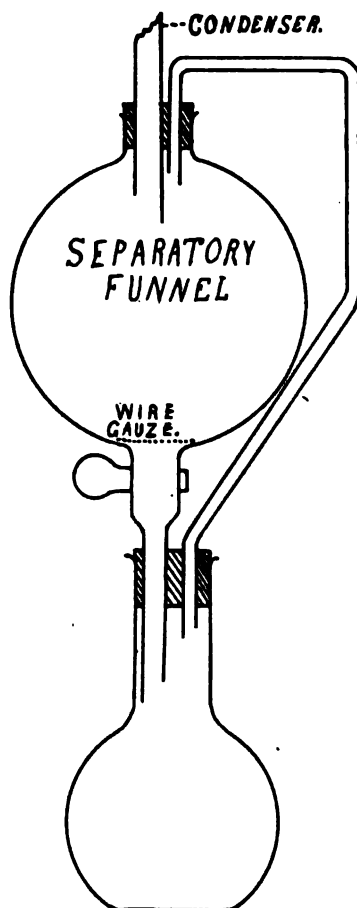
<sup>1</sup> *Am. J. Sci. and Arts*, 2nd series, 33, 313.

<sup>2</sup> *Compt. rend.*, 30, 38.

<sup>3</sup> "Analyse der Fette," 3rd ed., p. 535.

<sup>4</sup> "Chemical Analysis of Oils, Fats, and Waxes," p. 542.

above it contains a small amount of oleic acid. Allen,<sup>1</sup> while he does not give the composition of myrtle wax, says that it contains 0.12 per cent of free acid (in terms of palmitic acid). Bayberry



wax has been suggested and used<sup>2</sup> as a convenient source of palmitic acid so that the question of its composition becomes a matter of importance.

The following experiments were undertaken for the purpose of obtaining additional evidence on this question. The material used was obtained by us directly from the berries by extraction with

<sup>1</sup> "Commercial Organic Analysis," 3rd ed., Vol. II, Part 1, p. 169.

<sup>2</sup> Chittenden and Smith: *Am. Chem. J.*, 6, 218.

petroleum ether. The extractor used was devised from ordinary laboratory apparatus and worked so well that we append a sketch of it for the benefit of any one who has occasion to extract quantities of material larger than can be contained in a Soxhlet's extractor of ordinary size.

The following constants were obtained by the methods given in Lewkowitsch's "Chemical Analysis of Oils, Fats and Waxes."

Specific gravity, $\frac{22^{\circ}}{15.5}$ .....	0.9806
Specific gravity, $\frac{99^{\circ}}{15.5}$ .....	0.878
Melting-point.....	48° <sup>1</sup>
Solidifying point.....	45°
Saponification value.....	217
Iodine value (Hübl).....	3.9
Reichert-Meissl number.....	0.5
Acid number.....	30.7
Refractive index, 80°.....	1.4363

These figures show the absence of oleic and volatile acids and agree with the assumption that myrtle wax is mainly palmitin with some lower glyceride and a small amount of free acid. By crystallizing four times from petroleum ether pure palmitin was obtained, melting-point, 62.5; saponification value, 209.4; refractive index, 1.4380 at 80°.

Like most fats, myrtle wax shows a change of melting-point and other constants on standing. The berries from which the above wax was obtained were picked in September and the wax was extracted and its constants obtained in November. On extracting another portion in March, a melting-point of 54° was obtained. Wax from berries obtained in August and extracted in March melted at 55.4°. A redetermination in March of the melting-point of the main portion gave 52.5°, a rise of 4.5° in four months. A specimen of wax about four years old melted at 57° and solidified at 58.3°. These rather high figures led us to suspect that stearin might be present but, after repeated crystallization from alcohol, practically pure palmitin was obtained, melting at 61.5° and giving a saponification value of 206.7. The absence of stearic acid was finally shown by the fact that Hehner and Mitchell's method gave no stearic acid even on salting with a crystal of stearic acid and

<sup>1</sup> "Method of Allen," Vol. II, Part I, p. 34.

allowing to stand for a further period of ten hours at  $0^{\circ}$ . We conclude therefore that myrtle wax contains no stearin and that the high melting-point of the older material is due to the obscure change which takes place in many fats on standing. We hope to study this change in myrtle wax further and determine how the constants, other than melting- and solidifying-points, are affected thereby.

LEWIS INSTITUTE, CHICAGO, ILL.,  
March, 1903.

## THE ANALYSIS OF BRONZES AND BEARING METALS.<sup>1</sup>

BY H. E. WALTERS AND O. I. AFFELDER.

Received April 22, 1903.

In the laboratory with which the writers are connected, many bronzes and bearing metals are analyzed, and it was thought that the methods which are used might prove of interest to the members of this Section.

While the scheme contains much that is old, we wish to call particular attention to the volumetric method for determining lead, as the results obtained by it are as reliable as those obtained by the sulphate method.

### BRONZES.

The analysis of bronzes is carried out as follows:

Weigh 1 gram of the sample (0.5 gram, if the lead is over 15 per cent.) into a No. 2 beaker, cover with a watch-glass, add 10 cc. nitric acid (sp. gr. 1.42) and warm until all is dissolved. When in solution, add 40 cc. hot water and boil five minutes, filter, wash with 2 per cent. nitric acid, burn and weigh as  $\text{SnO}_2$ . To the filtrate add 25 cc. strong ammonia and heat to boiling, then add about 5 grams ammonium persulphate and boil from five to ten minutes. Make acid with sulphuric acid, filter and wash with hot water. The lead will remain on the filter as lead peroxide. Transfer the precipitate and filter to the beaker in which precipitation was made, add water and stir well to disintegrate the filter-paper. Dilute to 600-700 cc. with cold water, add about 3 grams potassium iodide and some starch solution. When all the iodide is dissolved, add 10 cc. hydrochloric acid (1:1), stir well and titrate

<sup>1</sup> Read before the Pittsburg Section of the American Chemical Society at the first monthly meeting, March 19, 1903.

with one-twentieth normal sodium thiosulphate until the solution changes from the dirty and dark yellow color to a bright lemon-yellow; or, an excess of sodium thiosulphate may be added and the excess titrated with one-twentieth normal iodine solution until the color changes from the bright yellow of the lead iodide present to the dirty and dark yellow. The number of cubic centimeters of sodium thiosulphate used multiplied by 0.5175 will give the percentage of lead. Where speed is not desirable, the lead may be determined by adding sulphuric acid to the filtrate from the oxide of tin, or the lead and copper may be deposited with the electric current.

Dilute the filtrate from the lead peroxide to 500 cc., heat to boiling and add 50 cc. of a 20 per cent. sodium thiosulphate solution,<sup>1</sup> boil five minutes, filter, wash with hot water, burn, and weigh as CuO.

Copper may also be determined by the following method, which is a modification of Low's method.<sup>2</sup> Dissolve 0.5 gram of the sample in 10 cc. nitric acid (sp. gr. 1.42). When in solution, dilute with cold water and add sodium carbonate until the solution is alkaline, make acid with acetic acid and add about 3 grams potassium iodide and some starch solution. Titrate with a sodium thiosulphate solution which has been standardized with pure copper.

Oxidize the filtrate from the copper sulphide thrown down by the thiosulphate as described above, with nitric acid and potassium chlorate and evaporate until the volume is about 300 cc. Make a basic acetate separation and determine iron or aluminum by the well-known methods. Make the filtrate from the iron or aluminum strongly alkaline with ammonia, heat to boiling and add ammonium persulphate, boil five minutes, filter, and wash with hot water, burn and weigh as  $Mn_2O_4$ .

To the filtrate from the manganese add ammonium phosphate in excess, heat to boiling and add hydrochloric acid until there is but a slight excess of ammonia, boil five minutes, filter and wash with hot water. The precipitate may be dried and weighed as  $ZnNH_4PO_4$ , or it may be filtered on a Gooch crucible and ignited to  $Zn_2P_2O_7$ . It may also be titrated with standard acid and alkali.<sup>3</sup>

<sup>1</sup> Nissenson and Neumann: *Chem. Ztg.*, 1895, p. 1591.

<sup>2</sup> *Eng. and Min. J.*, 1895.

<sup>3</sup> Walker: *This Journal*, 23, 468.

Any nickel which may be present will be found in the filtrate from the zinc and may be precipitated as sulphide and ignited to NiO. If manganese is present in small quantities, it may be determined in a separate portion by the following method: Weigh 0.2 gram of the sample into a suitable test-tube, add 10 cc. nitric acid (sp. gr. 1.20) and warm until the sample is dissolved and all nitrous fumes are driven off. Add 15 cc. silver nitrate solution (1.33 grams of the salt to 1 liter of water) and about 0.5 gram ammonium persulphate, warm until the manganese is oxidized to permanganic acid, cool, transfer to a beaker, dilute to 100 cc., and titrate with standard sodium arsenite or hydrogen peroxide until disappearance of the pink color.

#### DETERMINATION OF PHOSPHORUS.

To determine phosphorus dissolve 1 gram of the sample in 5 cc. fuming nitric acid, evaporate to expel most of the free acid, add 10 cc. concentrated hydrochloric acid and evaporate to dryness. Dissolve the residue in hydrochloric acid and water, heat to boiling and precipitate lead, tin, and copper with metallic zinc, filter and wash with hot water. To the filtrate add some iron solution free from phosphorus and 10 cc. nitric acid (sp. gr. 1.42), boil a few minutes and then precipitate with ammonia and filter to separate most of the zinc, dissolve the precipitate in hot nitric acid (sp. gr. 1.20) and precipitate the phosphorus with molybdate solution. The yellow precipitate may be weighed or titrated.

#### BEARING METALS.

If the sample is high in tin and low in lead, proceed as outlined for bronzes, but if the sample is high in lead and contains antimony, proceed as suggested by Mr. George Hopkins, chemist to the Carrie Furnaces of the Homestead Steel Works, he having found that the addition of an excess of pure tin will insure the complete separation of the antimony with the oxide of tin. Weigh 0.5 gram of the sample and 0.25 gram of pure tin into a tall No. 2 beaker, cover with a watch-glass, add 20 cc. nitric acid (sp. gr. 1.33) and boil down to pastiness, add 40 cc. hot water and boil a few minutes, filter and wash with 2 per cent. nitric acid, burn and weigh as  $\text{SnO}_2 + \text{Sb}_2\text{O}_3$ . The filtrate is made strongly alkaline with caustic potash and the lead oxidized by adding about 10

grams ammonium persulphate. The rest of the analysis is carried out as outlined for bronzes.

To determine antimony<sup>1</sup> weigh 1 gram of the sample and 1 gram potassium iodide into a No. 2 beaker, add 80 cc. hydrochloric acid (sp. gr. 1.10) and boil gently for one hour, filter on a weighed paper or Gooch crucible and wash with dilute hydrochloric acid and then with hot water until free from chlorides. Wash once with alcohol, dry for one hour at 100° C. and weigh. The increase in weight is metallic antimony. Calculate this to  $Sb_2O_3$  and subtract from the weight of the mixed oxides; calculate the tin from the weight of stannic oxide found and subtract the tin which was added.

Arsenic is determined in a separate portion by any of the well-known distillation methods.

Bismuth, if present, would be found with the copper sulphide, and can be determined by dissolving the sulphides in nitric acid, and precipitating the bismuth with ammonia.

#### REMARKS.

It will be noted that the filtrate from the tin in bronzes is made alkaline with ammonia, while in bearing metals, caustic potash is used. If caustic potash be used for bronzes, the copper would be precipitated and the lead would not be completely oxidized, while if the filtrate of a high lead-bearing metal is made alkaline with ammonia the lead hydroxide precipitate would be of such large volume that complete oxidation would not take place.

In filtering the lead peroxide it is necessary to add some paper pulp to the filter, otherwise some of the precipitate will run through. Should manganese be present, the lead will have to be determined by the sulphate method as the oxide of manganese would be precipitated with the lead peroxide and would not dissolve in the sulphuric acid added.

While we have not made many experiments, we feel safe in saying that the manganese could be separated directly from the copper sulphide filtrate, if most of the sulphuric acid is neutralized and the solution oxidized with ammonium persulphate.

In determining lead by the sulphate method or by the electrolytic method, a large amount of time is consumed in evaporating

<sup>1</sup> Andrews: This Journal, 17, 772.

to sulphuric fumes or in the long passage of the electric current, while by the titration method, if lead only is wanted, it may be determined without separating the tin, and the time required will be about thirty minutes.

If the copper is determined by the volumetric method, tin, lead, and copper results will be obtained in about one hour.

The following lead results were obtained on the same samples by the sulphate and volumetric methods.

Sample.	Sulphate method.	Volumetric method.
Bronze No. 4.....	2.60	2.61
" " 2.....	4.68	4.71
" H.....	5.05	4.97
" No. 1.....	5.39	5.33
" A.....	5.67	5.62
" B.....	7.47	7.51
" M.....	9.77	9.73
" S.....	13.72	13.62
" A.P.....	26.68	26.55
Babbitt C.....	3.29	3.41
" D.S.....	65.85	65.93
" L.....	80.80	80.73
" D.....	89.63	89.50

We have lately had occasion to determine sulphur in bronzes and we have done this by dissolving about 10 grams of the sample in the double chloride of potassium and copper used in carbon determinations, filtering off the sulphide of copper and igniting to copper oxide. We then calculate the sulphur from the weight of oxide found; of course, in very accurate work the copper sulphide should be oxidized and the sulphur determined as barium sulphate.

Following are some analyses made by the methods outlined in this paper. All precipitates obtained were tested and in no case were impurities found.

	Babbitt.	Babbitt.	Bronze.	Bronze.	Bronze.	Bronze.
Tin.....	4.13	43.27	7.41	4.85	7.88	3.55
Lead.....	79.30	43.63	9.73	2.80	5.05	5.87
Copper.....	....	0.56	82.09	90.31	85.68	86.23
Antimony.....	16.30	12.60	....	....	....	....
Zinc.....	....	....	0.95	....	1.46	3.55
Manganese.....	....	....	....	1.80	....	....
Iron.....	....	....	....	0.21	....	0.40
Sulphur.....	....	....	....	....	....	0.30
	99.73	100.06	100.18	99.97	100.07	99.90

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## SILVER AS A REDUCING AGENT.

BY W. S. HENDRIXSON.

Received March 24, 1903.

As has been pointed out, silver, in a finely divided condition, is dissolved by ammonia in the presence of atmospheric oxygen, and it slowly reduces a neutral solution of potassium permanganate.<sup>1</sup>

It occurred to the writer that it might be of interest to study in a systematic and quantitative way the behavior of finely divided silver toward substances that readily give up oxygen, such as chromic, chloric, bromic, iodic and permanganic acids. Thus far the action of silver on chromic, chloric and iodic acids has been studied and the results and related problems are of sufficient interest to make the author desirous of studying the subject somewhat exhaustively. It is deemed best, in view of the absence of aid and the small amount of time at his disposal, to give some of the results in this preliminary statement and reserve the details for a future communication.

Three separate preparations of silver were made, two from the ordinary commercial nitrate, and one, which was used in most of the following experiments, from pure silver obtained by the method of Stas. In each case the silver was precipitated from an alkaline solution of silver oxide by formaline. It was washed and heated alternately with ammonia and dilute sulphuric acid, and washed until every trace of the acid was removed. The preparations were dried and heated at various temperatures, from 125°, in one case, to low red heat in another.

*Action of Silver on Chromic Acid.*—A solution of potassium bichromate was prepared by weighing the salt which had been obtained by crystallizing three times from water the chemically pure salt of commerce, and drying to constant weight. The salt was heated for two hours in a porcelain crucible in an air-bath at 120°, and then during two-hour periods at 150°, 170°, 200° and 300°. The crucible was then placed upon a triangle in a large porcelain crucible which served as an air-bath and which was heated with the full burner flame for two hours, when the salt showed incipient fusion. Its weight remained perfectly constant above 200°, and 17 grams lost only a few milligrams above 120°. From this salt

<sup>1</sup> M. Carey Lea: *Ztschr. anorg. Chem.*, 3, 180.

and water obtained by fractionally distilling ordinary distilled water, a fifth-normal solution with respect to its oxidizing power was made, containing 9.8166 grams to 1 liter.

Weighed amounts of silver, about 1 gram in each case, were heated, sometimes in a covered beaker and sometimes in a flask with an air-cooling tube ground into its neck, with 25 cc. of the chromate solution and the same volume of normal sulphuric acid. Heated to gentle boiling, the time necessary for the complete reduction of the chromate varies much with the fineness of division of the silver. With silver used in the first two experiments the reduction was complete in fifteen minutes, while that used in 3, 4, and 5 required much longer. After the reduction was complete, the remaining silver was weighed in a Gooch crucible.

Following are the results of five experiments. The theoretical value is, of course, based upon the supposition that 1 molecule of chromate oxidizes 6 atoms of silver.

	Volume of bichromate. cc.	Silver dissolved.	Theory.
1.....	25.00	0.5413	0.5397
2.....	25.00	0.5428	.....
3.....	25.00	0.5380	.....
4.....	25.00	0.5366	.....
5.....	25.00	0.5376	.....

*Action of Silver on Iodic Acid.*—In experiment 6 the iodic acid and silver were heated with normal sulphuric acid and in 7 the iodic acid was in water solution. After heating at the boiling-point for about two hours, replacing the water evaporated from time to time, the undissolved silver, silver iodate and iodide were weighed. So much of the mixture as possible, without getting asbestos from the Gooch crucible, was transferred to a porcelain crucible, weighed and heated to redness. Oxygen was evolved and was determined by loss. From the loss of oxygen in a portion of the mixture, the silver as iodate could be calculated, and from this, the silver in solution and the silver taken, the silver as iodide could also be calculated. In the following, column 1 shows the silver used, 2 the total loss of oxygen, 3 silver as iodate, 4 silver in solution, and 5 silver as iodide.

	1.	2.	3.	4.	5.
6.....	1.3700	0.1418	0.3188	0.0434	0.0727
7.....	1.0225	0.1508	0.3390	0.0008	0.0727

In experiment 6, the ratio of silver as iodide to the total silver oxidized is 1:5.98 and in 7 the ratio is 1:5.67.

*Action of Silver on Chloric Acid.*—In experiment 8, 7 cc. of Merck's chloric acid were diluted to 50 cc., and such a solution was about three-tenths normal. The acid contained only a trace of hydrochloric acid, too small an amount in the volume taken to influence the result. In experiment 9, normal sulphuric acid and pure potassium chlorate were used. After heating about two hours, the silver in solution and the residue of silver and silver chloride were determined.

	Silver taken.	Silver in solution.	Silver as chloride.
8 .....	2.0295	0.8859	0.1775
9 .....	1.9517	0.5514	0.1473

In experiment 8, the ratio of the silver as chloride to the total silver acted upon is 1:5.99 and in 9 the ratio is 1:4.74.

The experiments show that both chromic and iodic acids are capable alone of oxidizing large quantities of finely divided silver. Both acids seem to react quantitatively upon silver with the result that a molecule of the acid is completely reduced and 6 atoms of silver are oxidized, 1 of which forms a halide and 5 form silver chlorate or iodate as shown in the equation



The action goes on in very dilute solutions. Calculations from the amounts of acids used and silver oxidized show that the strength of the iodic acid solution, when the experiment was stopped in experiment 7, could not have exceeded one-twentieth normal, and the strength of the chloric acid at the end of experiment 8 was about one-tenth normal. Bromic acid also readily dissolves silver but this reaction has not yet been quantitatively studied.

*Action of Dilute Sulphuric Acid on Silver.*—M. Carey Lea<sup>1</sup> has stated that even very dilute sulphuric acid dissolves, in small quantity, finely divided silver. I found this to be true in the case of every sample of silver prepared, and the amounts dissolved by the normal acid alone were determined. The weights of silver dissolved were in two samples about 0.4 milligram for each gram of silver taken, amounts so small that no corrections were made in experiments 1 to 8. A correction was, however, applied in experiment 9 in which the silver used was much more soluble.

<sup>1</sup> *Loc. cit.*

Since it was observed that continued heating did not seem to influence the amount of silver which the acid alone dissolved, a study was made of the reason for this solvent action. About a gram of silver on which the acid exerted a marked solvent action, was placed in a hard glass tube which was stoppered into a distilling flask so that the tip of the tube was in the bulb of the flask.

Through the tube and flask, which contained normal sulphuric acid and was placed horizontally, was passed pure hydrogen and the acid was boiled to expel any dissolved oxygen. The silver was heated in the current of hydrogen to reduce any oxide that it might contain. When cool it was allowed to fall into the boiling acid by tilting the flask and tube. By depressing the neck of the flask, small portions of the acid could be drawn off through the side tube from time to time and tested for silver. Though the evaporation was continued practically to dryness, no trace of silver was found in solution.

To determine whether the apparent solvent action might not be due to superficial oxidation of the silver, the above experiment was repeated, save that the silver was not heated. Again after long boiling no silver was found in solution. It then seemed of interest to determine at least approximately at what concentration boiling sulphuric acid begins to attack silver. The experiment was repeated save that the silver was not heated, and pure, dilute acid of the ordinary reagent strength was used. The acid was allowed to concentrate by evaporation and was, toward the end of the experiment, tested for silver at least every minute. Suddenly the character of the boiling changed and the silver rose to the surface and appeared spongy, owing to the formation of sulphur dioxide. The boiling was stopped and a test showed silver in solution. The acid was allowed to cool, a portion of it was weighed and titrated, and it showed a concentration of 74.03 per cent.

The above experiment seems to show definitely that dilute sulphuric acid alone is incapable of dissolving finely divided silver, and that the seeming solvent action is due to the oxygen of the air, oxygen dissolved in the acid, or to that derived from some external source.

In the near future an attempt will be made to ascertain whether, by excluding extraneous oxygen, the actual oxidizing power of a

bichromate solution may not be very accurately determined with silver.

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March 21, 1903.

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## REDUCIBILITY OF SOME METALLIC OXIDES BY HYDROGEN AND CARBON MONOXIDE.

BY IRVING W. FAY AND ALBERT F. SEEKER.

Received April 11, 1903.

In passing hydrogen gas over silver oxide in a bulb tube to show the reduction of the oxide to metallic silver I frequently noticed slight explosions and a sudden change of oxide to metal at what seemed a low temperature for such an effect. In the literature, I found that silver oxide was reduced by hydrogen at  $85^{\circ}$ <sup>1</sup> and  $100^{\circ}$ .<sup>1</sup> Wishing to test the accuracy of these temperatures, the following investigation was begun with the impression that both temperatures were too high. Both hydrogen and carbon monoxide were used to reduce the silver oxide. Later, other oxides were submitted to the reducing action of these two gases.

The method used by Mueller<sup>2</sup> consisted in placing a glass tube containing the oxide in the sand of a sand-bath. A thermometer was thrust into the sand so that the bulb was close to the part of the tube containing the oxide. The tube was bent at a right angle, one end sealed, the open lower end dipping under water. The tube was filled with hydrogen and the temperature increased. Reduction of the oxide was shown by ascent of water in the open end or arm of the tube.

Wright<sup>3</sup> and Luff placed the metallic oxides for reduction in a test-tube arranged vertically in a paraffin bath, about 0.5 gram being taken for each observation. The mouth of the test-tube was closed by a cork with three perforations, one for the thermometer, the bulb of which reached to the bottom of the tube, one for the entrance tube for leading in the pure gas, and the third for an exit tube just passing through the cork and bent at a right angle and coupled by a rubber joint to a Will and Varrentrapp's ammonia

<sup>1</sup> Wöhler: *Ann. Chem. (Liebig)*, 30, 4.

<sup>2</sup> Müller: *Pogg. Ann.*, 136, 51.

<sup>3</sup> *J. Chem. Soc. (London)*, 33, 1.

bulb apparatus filled with clear baryta water. In order to make sure that the entering gas was at the same temperature as the bath, the entrance tube was bent over, downwards and upwards, so as to form a U, reaching down to the bottom of the test-tube and lying close to the outer surface; the upper part of the tube was wrapped with lamp-wick to prevent aerial cooling. Loss of weight was used to determine actual reduction, and fifteen minutes was the time allowed for each test.

#### EXPERIMENTAL PART.

##### REDUCTION OF SILVER OXIDE BY HYDROGEN.

The oxide was that sold as chemically pure. As a preliminary test, silver oxide was placed in a tube about 0.25 inch internal diameter, so bent that it was easily clamped in position with the bend 1 inch below the surface of oil in an oil-bath. A thermometer was hung in the oil with its bulb close to the bend of the glass tube where the silver oxide lay. Hydrogen gas from zinc and hydrochloric acid without drying was passed slowly over the oxide. At a temperature of  $100^{\circ}$ , the oxide was reduced in a few minutes to the familiar grayish white powder of metallic silver. An hour's heating at  $80^{\circ}$  did not seem to reduce any oxide, but examination under a microscope showed metallic silver in the dark powder. At  $40^{\circ}$  the microscope revealed particles of silver. The silver oxide had previously been examined under the microscope, and metallic silver proved absent. Below  $40^{\circ}$  no reduction was apparent, but, suspecting that longer exposure to hydrogen would show a reduction, a quantity of oxide was sealed in an atmosphere of hydrogen within a tube and laid aside in a drawer at ordinary laboratory temperature. At the end of a week, the black color of the oxide was completely changed to white metallic silver, and moisture could be seen upon the glass inside of the tube. A similar tube similarly charged was placed alongside a block of ice in a refrigerator. In a week, the powder had become blacker, and moisture was shown by the powder sticking to the tube, and metallic silver was seen under the microscope.

To insure the constant maintenance of  $0^{\circ}$  C. during the test, a wooden V-shaped trough was used, 1 foot in length and about the same in height. The tube containing the oxide lay along the

bottom of the trough, the end projecting through a round hole so bored as to allow of easy removal and insertion of the oxide tube. Crushed ice was kept in the trough, and woolen coverings were placed over it.

Pure dry hydrogen gas was used for the subsequent work. It was made from zinc and sulphuric acid, to which some copper sulphate solution had been added, and it was further purified by passing it in succession through two wash-bottles containing permanganate of potash solution, a U-tube containing pumice saturated with a solution of mercuric chloride, a U-tube filled with pumice wet with a solution of potassium hydroxide, a piece of iron pipe, containing copper tacks and copper gauze, heated to redness (the wrapped ends kept cool by water dripping from capillary tubes), a U-tube containing anhydrous copper sulphate, a tower of calcium chloride, and a wash-bottle half-filled with phosphorus pentoxide. The rubber joints were covered with shellac varnish.

A glass tube 0.5 inch internal diameter was charged with silver oxide, and capillary tubes were drawn out at each end. The tube was placed in the ice trough and, when some time had elapsed to allow it to attain  $0^{\circ}\text{C}$ ., a stream of hydrogen was passed for one hour, and then a manometer tube consisting of a capillary tube of U-shape half-filled with mercury and so bent that the parallel arms were but an inch apart, the height of the manometer being 12 inches, was joined to the oxide tube by a short, tightly-fitting black rubber tubing, afterward covered with shellac varnish.

The capillary where the hydrogen had entered was sealed, and except for additions of ice from time to time, the apparatus was left to itself for five days. The progress of the reduction is shown in the following table of corrected readings.

Rise of mercury in the arm toward the oxide tube:

	mm.
End of 6 hours.....	7.6
" " 1 day.....	24.0
" " 2 days.....	35.8
" " 3 ".....	47.8
" " 4 ".....	56.4
" " 5 ".....	70.4

On removing the tube from the melting ice, moisture was plainly visible condensed on the upper side.

The amount of reduction was so much more than was expected

that it was feared hydrogen had diffused outward through the rubber joint, and thereby increased the apparent reduction. Another tube was prepared to test this by having the oxide tube and the capillary manometer entirely of one piece of glass. A long capillary tube was drawn out from the end of an 8-inch glass tube; it was then bent at a right angle and turned in U-shape, the parallel arms close together; another very short capillary was drawn out close to where the manometer capillary joined the main tube; this short second capillary on the same end as the manometer allowed a continuous stream of hydrogen to pass without disturbance of the mercury in the manometer. This tube was charged along the bottom with silver oxide, the open end drawn out to a capillary and then placed in the ice trough to acquire  $0^{\circ}$ .

A stream of pure dry hydrogen was passed for one hour, and several times the tube was rocked in such a manner as to bring the mercury close up to the short capillary, through which hydrogen was passing. This accomplished the expulsion of all air in the branch of the manometer tube next the oxide. The capillaries at both ends were sealed and the tube maintained at  $0^{\circ}$  for twelve days by an abundance of ice and careful covering.

The amount of reduction day by day was as follows:

	mm. corrected.	
End of 6 hours.....	5.6	
" " 1 day.....	14.9	
" " 2 days.....	18.3	
" " 3 ".....	36.1	During the sixth day the apparatus was placed out of doors, when the temperature was $20^{\circ}$ below freezing.
" " 4 ".....	39.0	
" " 5 ".....	51.1	
" " 7 ".....	67.9	
" " 8 ".....	68.5	
" " 9 ".....	78.9	
" " 10 ".....	88.8	
" " 11 ".....	94.5	
" " 12 ".....	107.2	

Auric oxide, subjected to exactly similar treatment with hydrogen gas at  $0^{\circ}$ , showed a more rapid reduction than silver oxide, as the following table will show.

	mm.
End of 6 hours.....	67.8
" " 1 day.....	73.9
" " 2 days.....	66.4
" " 3 ".....	73.5
" " 4 ".....	80.0



In all of these tests the surface-tension of the mercury in the capillary manometer was such that movement was sluggish, and the tube needed frequent tapping to cause a readjustment of the mercury column.

#### REDUCTION OF THE OXIDES OF MERCURY BY HYDROGEN.

The oxide was placed in a glass tube 0.25 inch inside diameter, bent at such an angle that the bend itself was 1.5 inches below the surface of oil in an oil-bath, in which it was heated. At first, on passing the hydrogen, the temperature was rapidly increased until the oxide could clearly be seen to exhibit reduction. A thermometer was hung in the bath with its bulb close to the bend of the tube where the oxide lay. To determine the lowest temperature at which six hours' contact with hydrogen would show reduction, tests were made with fresh portions of oxide at each interval of  $5^{\circ}$  below the temperature discovered in the above process, and reduction proved by the vacuum formed within the tube. Each test was as follows: The ends of a glass tube 0.5 inch in diameter and 6 inches long were drawn out to capillary tubes 3 inches long. The oxide was introduced and spread along the bottom of the tube and a large excess of pure hydrogen passed through. Both capillaries were sealed and bent upward to allow of immersion in an oil-bath of moderate size. A constant temperature was maintained by a thermostat, and careful protection of the flame and bath from drafts. Any reduction at the end of the six hours' heating revealed itself by a partial vacuum formed within the tube when cooled to its original temperature.

To ascertain the presence of a slight vacuum and therefore of the slightest reduction of the oxide, a manometer was used, consisting of two capillary glass tubes fastened side by side to a millimeter scale, their lower ends joined by rubber tubing. The oxide-tube to be examined was connected by a small rubber tube to one arm of the manometer, *i. e.*, the capillary tube, scratched with a file near the tip, was thrust into the rubber tube, the other end of which was joined to one arm of the manometer. The mercury in both arms was brought to a level, the tip of the oxide tube broken off within the rubber tube, and any partial vacuum was at once revealed by a rise of the mercury in the arm of the manometer next to the oxide-tube. Blank tests made at different times showed

the largest error due to manipulation to be 5 mm. No metallic oxide was regarded as showing reduction unless the corrected vacuum attained exceeded 5 mm. The lowest temperatures for the reduction of the oxides of mercury are as follows :

Mercurous oxide.....	80° C.
Yellow mercuric oxide..	50° C., at 130° C. <sup>1</sup>
Red mercuric oxide.....	115° C., at 230° <sup>1</sup>

#### REDUCTION OF SOME METALLIC OXIDES BY CARBON MONOXIDE.

The method consisted in passing pure dry carbon monoxide over the metallic oxide charged in a bent glass with the bend immersed 1.5 inches below the surface of the oil in an oil-bath. The thermometer bulb was fixed close against the bend of the immersed tube where the oxide lay. A constant temperature at any degree was secured by a thermostat, and protection of the flame and oil-bath from drafts. Any carbon dioxide formed by reduction of the metallic oxide was detected by passing the gas through a Marchand tube, containing a solution of barium hydroxide.

The carbon monoxide was made from coarsely crushed potassium ferrocyanide and concentrated sulphuric acid. Raising the temperature rapidly until evolution of the gas began and then lowering the flame, gave perfect control of the gas, which otherwise may be given off tumultuously. The gas was purified and dried by passing it through a train consisting of two wash-bottles of solutions of sodium hydroxide and one of lime-water, a tower of calcium chloride, and a wash-bottle half-filled with phosphorus pentoxide. The barium hydroxide solution, one-third the strength of saturation, was shaken with barium carbonate to increase its sensitiveness to carbon dioxide. This solution was found sensitive to the carbon dioxide in 0.25 liter of atmospheric air, which is 0.075 cc. Lime-water was much less sensitive, requiring 0.75 liter of atmospheric air to give an equal amount of turbidity in the same volume of liquid. Efficiency of the purifying train was proved by making blank tests from time to time. The Marchand tube containing the solution of barium hydroxide was protected from backward diffusion of carbon dioxide from the air by a second Marchand tube, charged like the first. Each test was continued for six hours, the gas passing at the rate of one to two

<sup>1</sup> Müller: *Pogg. Ann.*, 136, 62.

bubbles per second, the temperature kept constant during the time. A first test was made sufficiently high to find where reduction actually took place with rapidity, then successive tests at intervals of  $5^{\circ}$ , until no turbidity was shown by the barium hydroxide solution. In reductions by carbon monoxide, a tendency clearly exists for the carbon dioxide formed to unite with unchanged oxide to form carbonate to some extent, but, with an excess of carbon monoxide passing, this, it is believed, could have but little effect upon the result.

The following shows reduction temperatures for carbon monoxide. (Time of test, six hours.) Silver oxide,  $0^{\circ}\text{C}.$ ; auric oxide,  $0^{\circ}$ ; mercurous oxide,  $0^{\circ}$ ; yellow mercuric oxide,  $0^{\circ}$ ; red mercuric oxide,  $95^{\circ}$ .

#### CONCLUSIONS.

(1) The minimum temperature of reduction of both silver and gold oxide by hydrogen is much below zero, and that for carbon monoxide lower than that for hydrogen.

(2) Carbon monoxide is a more rapid and efficient reducing agent than hydrogen.

(3) The differences in the temperatures of reduction of the yellow and red oxides of mercury make them exhibit properties of two different substances, and confirm the differences previously found in their behavior to chlorine,<sup>1</sup> oxalic acid,<sup>2</sup> iodic acid,<sup>3</sup> and ammonia.<sup>4</sup> Further work is being done with the oxides of lead and copper.

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#### NOTES.

*Analysis of Water from Hinton, West Virginia.*—This water is characterized by a large content of manganese, nickel and cobalt salts. In many mineral waters, manganese salts are reported as present in traces or in comparatively small quantities, but in this water the amount of manganese salts is so large that during evaporation a very marked brown precipitate of a

<sup>1</sup> Pelouze : *Compt. rend.*, 16, 50.

<sup>2</sup> Millon : *Ann. Chem. (Liebig)*, 18, 349.

<sup>3</sup> Rammelsberg : *Pogg. Ann.*, 44, 570.

<sup>4</sup> Hirzel : *Ann. Chem. (Liebig)*, 84, 258; Weil : *Pogg. Ann.*, 123, 358.

manganese compound is formed, part of which floats on the surface of the evaporating water. This precipitate dissolves on the addition of hydrochloric acid with the evolution of chlorine in such quantity that the evaporation of the acidified water to dryness cannot be made in a platinum dish.

The relative quantity of manganese salts in this water is greater than that in any of those given in Peale's<sup>1</sup> Mineral Springs of the United States, while the quantity of the nickel and cobalt salts is only exceeded by the amounts in the waters of the Jordan<sup>2</sup> Alum and Rockbridge Alum Springs, Virginia.

Still larger contents of manganese, nickel and cobalt salts are found in the water of Roncegno,<sup>3</sup> South Tyrol.

The specific gravity of the Hinton water at 15°-16° was 1.007.

The weight of solids dried at 180° was 1.2836 grams per liter, or 74.9750 grains per U. S. gallon.

The results of the analysis were:

	Parts to 1,000,000.
Potassium (K).....	4.6
Sodium (Na).....	306.7
Calcium (Ca).....	89.6
Magnesium (Mg).....	42.4
Aluminum (Al).....	1.3
Iron (Fe).....	10.5
Manganese (Mn).....	40.7
Nickel and cobalt (Ni, Co).....	3.6
Silicate ion (SiO <sub>3</sub> ).....	16.0
Carbonate ion (calculated) (CO <sub>3</sub> ).....	109.1
Chlorine (Cl).....	627.2
	<hr/>
	1251.7

This corresponds to:

	Grams per liter.	Grains per U. S. gallon.
Potassium chloride.....	0.0087	0.5082
Sodium chloride.....	0.7785	45.4722
Calcium chloride.....	0.1776	10.3736
Magnesium chloride.....	0.0847	4.9473
Magnesium carbonate.....	0.0710	4.1471
Alumina.....	0.0024	0.1402
Silica.....	0.0128	0.7476
Ferrous carbonate.....	0.0215	1.2558
Manganese carbonate.....	0.0848	4.9532
Cobalt and nickel carbonates.....	0.0073	0.4264
	<hr/>	<hr/>
	1.2493	72.9716

W. G. BROWN.

<sup>1</sup> Bulletin of the United States Geological Survey, No. 32.

<sup>2</sup> *Loc. cit.*, pp. 62 and 65.

<sup>3</sup> Gläser und Kalmann: *Ber. d. chem. Ges.*, 21, 1637 and 2679; abstract in *J. Chem. Soc.* (London), 84, 796 and 86, 28.

## NEW BOOKS.

**ON THE "BECKMANN REARRANGEMENT."** BY JULIUS STIEGLITZ, Professor of Chemistry in the University of Chicago. Chicago: University of Chicago Press. Price, 25 cents.

This is a carefully prepared monograph on the probable cause and mechanism of the "Beckmann Rearrangement," which is so defined as to include a variety of reactions in which an alkyl or aliphyl group leaves a carbon atom to attach itself to a neighboring atom of nitrogen, as well as the corresponding rearrangement in the case of oximes. The author, after arriving at the conclusion that "The interpretations of the rearrangement given by Hoogewerff and van Dorp, Hantsch, Beckmann, Hesse, Freundler, and Nef do not agree with all the established facts," advances evidence in support of the view, that "All the most important results of the investigations of the reaction from the point of view of the constitution of the substances involved, agree best with an interpretation which postulates the intermediate formation of a univalent nitrogen derivative as the essential cause of the rearrangement"

S. P. MULLIKEN.

**THE ANALYSIS OF OILS AND ALLIED SUBSTANCES.** BY A. C. WRIGHT, M.A., B.Sc. New York: D. Van Nostrand Co.; London: Crosby, Lockwood and Son. 8vo. Cloth, 241 pp. Price, \$3.50 net.

This book describes very fully the various constituents of oils, waxes and resins and also the methods of the determination of the physical and chemical properties of these bodies. It discusses further the treatment of the non-fatty matters contained in oils and gives the means of their identification and estimation. This is followed by the description, properties and methods of investigation of the important oils, fats and waxes, some fifty in number. The work concludes with the examination of some commercial products, as turkey-red oils, lubricating oils and greases, and paint oils.

The treatise, which may be tersely described as an abridged Lewkowitsch, is most admirable, and will doubtless replace it in many cases. There are, however, some statements which are not in accord with the usual experience, particularly that the open flash test of oils is better than the closed. In some instances the

methods are not explained with sufficient clearness ; one is in doubt, for example, as to the procedure to be followed in the estimation of free acid.

In view of the fact that all references are so far as "possible to the *Journal of the Society of Chemical Industry*, to which practically all chemists and students have access," it would seem to be of doubtful expediency to introduce into this book processes there given, the results of which are open to question, such as Farnsteiner's method for the separation of oleic acid. While the writer cordially concurs in the exclusion of some tests—particularly color tests—yet he feels that it was a mistake not to have included McIlhiney's bromine test, one of the most valuable in the examination of these compounds. The omission of the satisfactory David's test for rape seed oil is also to be noted. No mention is made of corn or peanut oils, although maize and earthnut oils are carefully described ; the treatment of linseed oil is particularly satisfactory.

Mineral oils, except as adulterants, are not discussed, although a description of the flash and viscosity tests is given. The usefulness of the work would be increased were the index more complete. It is a valuable book and may be warmly recommended to those interested in the subject.

A. H. GILL.

**A HISTORY OF HINDU CHEMISTRY FROM THE EARLIEST TIMES TO THE MIDDLE OF THE SIXTEENTH CENTURY A. D.** With Sanskrit Texts, variants, translation and illustrations. BY PRAPHULLA CHANDRA RAY. Vol. I. London and Oxford : Williams and Norgate. 1902. pp. i-iii, a-d, i-xxxix, 1-176, 1-41. 7 plates. 8vo. Price, 12s, 6d.

The author, who occupies the chair of chemistry in Presidency College, Calcutta, has done for Hindu chemistry what Berthelot did a few years ago for Greek, Arabic and Syriac documents of the Middle Ages. His historical studies begin with the sacred books of very early, uncertain dates, and extend to about the year 1550 A.D.; the second volume will probably bring the subject down to the present time. In the Atharva-veda, the Charaka and the Susruta, occur the earliest references to therapeutical and chemical knowledge, as well as to pharmaceutical preparations ; they date probably prior to the fifth century. In these and succeeding writings, alchemical ideas abound, mixed up with magic, sorcery, and religious rites of a debasing character. The chief of these were

known to the Arabians at an early date and furnished them with a large part of the chemical skill with which they are usually credited.

Hindu ideas concerning the constitution and properties of matter resemble in many points the philosophy of the early Greeks, and it has been suggested that the latter were influenced by Indian thought through Persia. Almost all the doctrines ascribed to Pythagoras, mathematical, religious and philosophical, were known in India in the sixth century B. C.

The invention of the processes of calcination and distillation is ascribed to the renowned and venerable Nagarjuna, one of the twenty-seven alchemists named in the *Rasaratnasamuchchaya*, a famous work of the Iatro-chemical period. Another philosopher in physical science was Kanāda who propounded a doctrine similar, in many points, to the atomic theory of Democritus; his anticipations as respects the propagation of sound and the identity of light and heat excite wonder and admiration.

The volume contains summaries of the knowledge of the ancient Hindus concerning metals, salts, alkalies (the "good" and the "bad"), and of technical arts having a chemical basis, such as the manufacture of calomel, of saltpetre, as well as of metallurgical operations.

Zinc was recognized as a metal as early as 1374 A. D., long before pseudo-Basil Valentine, and Paracelsus.

The method of treating the refuse and wastage of goldsmith's workshops is described and explained in modern chemical language.

The claim is made that the Hindus knew how to prepare mineral acids earlier than Europeans.

To analyze the work more fully in the space that can be given is impossible; the whole book shows the erudition and careful study of an accomplished scholar, not only in chemistry but in Sanskrit as well, citations being given in this language.

An appendix contains several full page plates of furnaces, copper smelting, alum manufacture, etc.; also 41 pages of Sanskrit texts and two indexes, one to proper names and one to subjects [but why separated?].

The book bears internal evidence of having been printed in Calcutta, with clear type and on good paper. The second volume will be awaited with interest, and the two will form the standard

monograph on Hindu chemistry that will be indispensable in every library.

HENRY CARRINGTON BOLTON.

**THE TESTING OF CHEMICAL REAGENTS FOR PURITY.** BY DR. C. KRAUCH, chemist to the firm of E. Merck, Darmstadt. Authorized translation of the Third Edition by J. A. WILLIAMSON and L. W. DUPRÉ. With additions and emendations by the author. London: Maclaren & Sons; New York: D. Van Nostrand Co. 350 pp. 1903. Price, \$4.50 net.

To prescribe a series of tests of chemical reagents which should be sufficiently detailed to cover their use in all sorts of highly specialized cases would be well-nigh impossible. The general and many of the special applications of the inorganic reagents and of such organic substances as are employed as solvents, indicators, or for special tests are, however, well provided for in the material which Dr. Krauch has compiled from various sources, and to which he has added the results of his own experience. For each substance the Latin name, symbol, molecular weight, and a brief description are given, and these are followed by discussions of the tests for impurities, the methods of quantitative estimation, the uses of the reagent, precautions to be observed in connection with its storage, and a description of its commercial varieties. An appendix includes the preparation of ordinary reagents and of normal solutions, a discussion of reagents and reactions in general, and a table of atomic weights [which, however, bears the date, 1890].

The translation seems to have been faithfully carried out. It may be questioned whether it would not have been preferable to add the references to English works and journals to those in other languages, rather than to substitute them, since the reader may often prefer to consult the original papers. The Lunge and Isler table for the strength of sulphuric acid at various densities is stated on page 309 to be more reliable than that of Kolb and it would seem that it should replace the latter table in this work.

To many who have found the German edition of Dr. Krauch's book a valuable assistance, this translation will need no endorsement; to others it can be recommended as a guide in determining the extent to which freedom from impurities in reagents may reasonably be expected, and in the selection of methods of testing.

H. P. T.



**LEAD AND ITS COMPOUNDS.** BY THOMAS LAMBERT. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1902. 228 pp. Price, \$3.50.

Some seventy pages of this book are taken up with a description of the dressing of lead ores and the metallurgy of lead.

A chapter on lead oxides and their manufacture follows, and fifteen pages are devoted to substitutes for white lead. A brief account of the metallurgy of zinc follows, including a description of compounds used as pigments, and of purrce stone, china clay, etc.

Drying oils, siccatives and turpentine are briefly discussed. A classification of mineral pigments and a chapter on the analysis of raw and finished products close the book. The tables at the end are of little moment.

Inasmuch as this book contains nothing which is not more fully and authoritatively treated in other easily accessible works, it can be of little use to the American chemist or metallurgist, but is evidently designed to contain general information of interest to those engaged in the manufacture of paint from lead and zinc compounds.

WM. HOSKINS.

**TESTS AND REAGENTS, CHEMICAL AND MICROSCOPICAL, KNOWN BY THEIR AUTHORS' NAMES,** together with an Index of Subjects. BY ALFRED I. COHN, PH.G. New York: John Wiley & Sons. 1903. 8vo. Cloth. 353 pp. Price, \$3.00.

The object of this book, as stated by its author, is "To supply the busy chemist, microscopist, and pharmacist with data which are frequently desired, but which are often not at hand or are inaccessible." The tests and reagents are arranged alphabetically under the names of their originators. Their number is estimated to be not far from 2,500. The descriptions are necessarily all very compact, but the work of condensation has been well done—a fact which in a measure compensates for the usual omission of bibliographical references.

The following selected topics will serve to illustrate the nature of the matter abstracted: Hager, "Test for Dextrine in Acacia"; Halphen, "Cottonseed Oil"; Hammersten, "Indican in Urine"; Haug, "Decalcification Solution"; Hefelmann-Mann, "Fluorine in Beer"; Hayem, "Solution for Fixing Blood Corpuscles."

The book is especially complete in its list of tests and reagents

employed in pharmaceutical and medico-chemical practice, but contains much to make it a useful addition to the library of any analyst. Its value is greatly enhanced by the addition of the alphabetical subject index.

S. P. MULLIKEN.

VORLESUNGEN ÜBER THEORETISCHE UND PHYSIKALISCHE CHEMIE. VON J. H. VAN'T HOFF. Zweites Heft. Die Chemische Statik. Zweite Auflage. Braunschweig: Friedr. Vieweg und Sohn. Ladenpreis, geheftet, Mk. 4.

The second edition of the second part of this set of lectures differs very slightly from the first edition, the differences being mainly in choice of illustrative examples cited in the text, for which recognition of more recent work calls, and in the increased number of references. The chapter on solid solutions is the most conspicuous in both respects. A few typographical slips occur in the second edition which do not appear in the first, and curiously enough the second edition omits the references to Brunis' work (pages 68 and 70) mentioned in the text, though the reference is given in the first edition. The leading of the tables in the second edition seems to be an improvement, and the press work as a whole is quite satisfactory. The few changes made in this new edition of a well-known work do not justify any extended or detailed notice, but the opportunity can not be passed of insisting upon the great value of this work to the general chemist.

Considering chemical statics under the three general headings, Molecular Weights, Molecular Structure, and Molecular Grouping, the author has discussed the modern theory of solutions, gaseous, liquid and solid, stereochemistry, and physical crystallography, subjects usually treated as widely variant in character, and with but incidental points of contact, but which are here brought into a comprehensive whole. There are probably few indeed who will not find their mental horizon considerably widened by the careful reading of this volume, and with its two companion ones on "Chemical Dynamics" and "The Relations between Properties and Composition" it should well repay an occasional re-reading.

FRANK K. CAMERON.

ELEMENTS OF PHYSICS. BY ERNEST J. ANDREWS and H. N. HOWLAND. With Manual of Experiments. New York: The Macmillan Company. 1903. Price, \$1.10 net.

The general plan of this new addition to the large number of

elementary texts on physics is "to eliminate a few subjects which have no practical bearing, and the relations of which to the fundamentals cannot well be made apparent; to present difficult subjects fully and in simple terms; and to connect each subject, directly or indirectly, with every other by fundamental principles or their corollaries."

This plan has been carefully and conscientiously followed and the resulting book is on the whole to be recommended. The weakest part is the "Manual of Experiments," but as most schools use a separate manual, this cannot be accounted a serious defect.

C. E. LINEBARGER.

**A TEXT-BOOK OF ORGANIC CHEMISTRY.** BY DR. A. F. HOLLEMAN. Translated from the Second Dutch Edition by A. JAMIESON WALKER, PH.D., assisted by OWEN E. MOTT, PH.D., and with the coöperation of the author. New York: John Wiley & Sons. 1903. 72 figures. Cloth. 8vo. xvii + 535 pp. Price, \$2.50.

The purpose of the author is to bring out distinctly the underlying principles upon which the division of the subject is based, the experimental proof for the constitutional formulas assigned, the bearing of physico-chemical theories upon the problems of organic chemistry, and the like, rather than to describe a large number of compounds or record a confusing mass of isolated facts; in a word, to provide a text-book which should give a clear presentation of the theoretical aspects of organic chemistry, rather than a condensed "Beilstein." The author's purpose has been carried out with very satisfactory results in the present work, an excellent text-book, widely and favorably known, this new edition being as nearly up-to-date as can reasonably be expected of any text-book. A second German edition has already appeared of the work, and an Italian translation is in preparation; English-speaking students will therefore be grateful to Messrs. Walker and Owen for this translation of the latest Dutch edition. The publishers' work is well done, the book being gotten up in very attractive form, clearly printed on good paper.

MARSTON T. BOGERT.

**SIDEROLGY: THE CONSTITUTION OF IRON ALLOYS AND SLAGS.** BY HANNS FREIHERR VON JUPTNER. Translated from the German by CHARLES SALTER. London: Scott Greenwood & Co.; New York: D. Van Nostrand Co. 1902. viii + 344 pp. Price, \$5.00.

The original edition of this book has been reviewed in this.

Journal (23, 117); in the present review we shall speak only of the translation. The translator has proved the exception to all rules, and has omitted a preface of his own. Perhaps under the circumstances it would be well to be charitable, and forgive some of the faults of the book, inasmuch as we are not informed of the conditions under which it has been produced. It is impossible, however, not to mention some of them.

The translation is similar to the original in all respects, with the single exception of the valuable bibliography which appeared at the end of the original. This has unfortunately been omitted in the translation. In the second volume the author included much valuable material on the application of the phase rule to the equilibrium phenomena of iron and carbon, which had been published by Roozeboom, Le Chatelier, and others after the first volume had appeared. As this will, ultimately, be included as part of the first volume by Jüptner, it seems a great pity that the translator did not see fit to incorporate it in its proper place.

On reading carefully through the book one is confronted by many inaccuracies, either original or copied from the German edition, which seems to indicate that the translator has not brought that love of duty, and knowledge of his subject to his aid which would provide a translation worthy of the original. It would be idle to mention all of the mistakes noticed, but some of the most striking will be referred to.

In regard to proper names, we find on page 10, *Gouthrie*, which should read Guthrie, copied from the original; on page 86, Sorby reads Storby; and E. D. Campbell appears in several places bearing the initials E. W. The terms inter-crystalline and inter-granular which originated with Stead in England, reappear in English as *intra*-crystalline and *intra*-granular; crystallites become crystal-liths. In the text the spelling pearlite is used, while the German *perlite* is used to designate the micrographs of this constituent.

The translation of some of the German words is particularly unhappy. Speaking of boring steel under water to collect the gases, anbohren is translated *broached*; uebergiesst as *suffuses*; zerhacktes as *hacked-about*; Glimmer ähnlich Blättchen as *scales analogous to mica*; gedacht, as *imagined*; Bestandtheile, as *compound*. Many other such mistakes are noticed.

It is to be regretted that so many evidences of carelessness are noticeable, but even with these the book is sure to be welcomed by those who are unable to read the original, and who are interested in the scientific treatment of the constitution of iron and its alloys. The book comes from the press in very attractive form, but the reviewer can see no reason why the reader should be forced to accept with it thirty-five pages of advertising matter. HENRY FAY.

**PHYSICO-CHEMICAL TABLES FOR THE USE OF ANALYSTS, PHYSICISTS, CHEMICAL MANUFACTURERS AND SCIENTIFIC CHEMISTS.** BY JOHN CASTELL-EVANS, F.I.C., F.C.S., Superintendent of the Chemical Laboratories and Lecturer on Inorganic Chemistry and Metallurgy, at the Finsbury Technical College. Volume I, Chemical Engineering and Physical Chemistry. London: Charles Griffin and Co., Lim.; Philadelphia: J. B. Lippincott Co. 1902. xxxii + 548 pp. Price, \$8.00.

This volume contains not only what its title in the narrower sense denotes—the physical constants of chemical substances, but also the values of various mathematical functions and of the relations of units in different systems, data pertaining to materials used in construction, and tables of many original calculations made by the author with the purpose of facilitating reductions and corrections and avoiding interpolations or calculations from empirical formulas. Most of the important quantities are expressed both in English and in metric units. The principal physico-chemical constants included in this volume are specific volumes and gravities and heat-expansions; specific heat-capacities and heats of fusion, vaporization, and solution; compressibilities; vapor-pressures; boiling-points, and melting-points.

The two most striking defects of the book revealed by a cursory examination are the absence of references to the original literature and the utter disregard of the significance of figures; thus in the mathematical tables many functions are given with three to seven more digits than the corresponding argument, and in the physical tables compressibility-coefficients are given with three or four figures when the unit is the atmosphere, with seven when the unit is the kilo per square millimeter or the ton per square inch, and specific heat-capacities and vapor-pressures are given with six figures, though the results of different investigators vary greatly in the fourth figure, etc.

In spite of these defects the book contains an enormous mass of data

within a small compass and in a form ready for practical use, and it may therefore prove of considerable value to industrial chemists and to chemical engineers. Scientific workers, however, will undoubtedly still prefer to utilize the original values of physico-chemical constants so well reproduced in Landolt and Börnstein's Tabellen, and to obtain mathematical functions from some work, like Holman's excellent Computation Rules and Logarithms, devoted especially to them.

A. A. NOYES.

ANNUAIRE POUR L'AN 1903, PUBLIE PAR LE BUREAU DES LONGITUDES.  
Paris: Gauthier-Villars. 24mo. 666 + 96 pp. Price, 1 fr. 50.

One-half this annual is occupied by astronomical data, one-quarter by diverse information of the nature of a newspaper almanac, and the last quarter by miscellaneous physical and chemical tables. The latter are either so incomplete or so antiquated in their data as to be in most cases no better than none at all. Even in a table of gaseous densities contributed by Berthelot, are to be found such serious mistakes as mercury and cadmium vapors being given the formulae  $Hg_2$  and  $Cd_2$ . Cheap book—unreliable information, at least as far as the physical and chemical tables are concerned.

J. W. RICHARDS.

A CATALOGUE OF THE LIBRARY OF THE CHEMICAL SOCIETY [OF LONDON].  
Arranged according to authors with a subject-index. London: 1903.  
12mo. 324 pp.

This excellently printed volume shows on every page due care in its preparation, will admirably serve the purpose for which it has been compiled, and will prove useful to all interested in the bibliography and history of chemistry. Those handling it should bear in mind that it is a catalogue of the books in a given place and not a bibliography, and the absence of a book of intrinsic merit must not be criticized. To condemn a catalogue for its omissions is hardly just, when all the compiler can do is to include the books on the shelves of the library even though he may feel the need of certain volumes more keenly than the members of the Society themselves do.

The compiler of this volume, Mr. Robert Steele, deserves the thanks of all chemists and librarians.

HENRY CARRINGTON BOLTON.

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## Proceedings.

### COUNCIL.

The Council has approved the establishment of a local section to embrace the territory covered by a ten-mile radius from Cornell University, Ithaca, N. Y., with headquarters at Cornell University, to be known as the Cornell Council.

#### MEMBERS ELECTED BETWEEN NOVEMBER 28 AND DECEMBER 26, 1902.

- Beatty, Leon O., 606 W. 113th St., New York City.  
Beggs, H. C., 5631 Butler St., Pittsburg, Pa.  
Bishop, Howard H., 609 Greene Ave., Brooklyn, N. Y.  
Bole, Wm. S., Bozeman, Mont.  
Bonsall, James M., Dover, N. J.  
Brown, Ernest W., 911 North Carolina Ave., S. E., Washington, D. C.  
Brown, James V., Jr., 1063 Congress St., Chicago, Ill.  
Brumbaugh, E. Vane, Fayette, Iowa.  
Buel, Hambden, South Pittsburg, Tenn.  
Butler, Chauncey E., 4548 W. 33d Ave., Denver, Colo.  
Cox, Irving J., 525 N. 5th St., Terre Haute, Ind.  
Davidson, Jesse A., Bozeman, Mont.  
Dyer, Kirk W., Pasadena, Cal.  
Falk, Milton J., 16 E. 81st St. New York City.  
Ferrero, Felice, 227 E. 58th St., New York City.  
Flaherty, Wm. A., Bozeman, Mont.  
Finley, Dozier, 1929 Russell St., Berkeley, Cal.  
Goessmann, L. E., 89 N. Munn Ave., East Orange, N. J.  
Goodell, Joseph E., 3132 Broadway, New York City.  
Gray, Geoffrey A., 3 So. Auburn Ave., Cincinnati, O.  
Hills, Franklin G., 1119 S. Union Ave., Pueblo, Colo.  
Hird, John D., Health Department, Washington, D. C.  
Kee, William J., Jr., Merrimac Chem. Co., North Woburn, Mass.  
Kinney, Charles T., Danville, Ill.  
Kraus, Edward H., 907 E. Adams St., Syracuse, N. Y.  
Lenk, Walter S., 205 Dryden Road, Ithaca, N. Y.

Lindmueller, Charles, Ohio Farmers' Fertilizer Co., Columbus, O.

Meyer, Franz, 68 Broad St., New York City.

Miller, Erwin H., 3504<sup>1</sup>/<sub>2</sub>, Vermont Ave., Los Angeles, Cal.

Miller, J. Strother, Jr., 409 B St., N. E., Washington, D. C.

Mitchell, Frank H., Orono, Me.

Patten, Harrison E., 1109 University Ave., Madison, Wis.

Plath, Dr. Gottfried, Sophienstrasse 8-lf., Charlottenburg-Berlin, Germany.

Popper, Edwin, 260 W. 93rd St., New York City.

Schreiner, Oswald, Delavan, Wis.

Stehman, John V. R., Birdsboro, Berks Co., Pa.

Tilkie, Charles M., Peter Cooper Glue Factory, Brooklyn, N. Y.

Vivian, Alfred, 244 W. 10th Ave., Columbus, O.

Wilson, Elbert S., 306 E. Yates St., Ithaca, N. Y.

Winter, Frank C., 636 W. Adams St., Los Angeles, Cal.

Wright, Charles E., Platteville, Wis.

#### CHANGES OF ADDRESS.

Archibald, E. H., Macdonald Chem. Bldg., McGill Univ., Montreal, Canada.

Arnold, Fred. N., Jr., The N. K. Fairbank Co., 225 E. 19th St., Chicago, Ill.

Burck, C. A., Iola Portland Cem. Co., Iola, Kans.

Chace, E. M., Bureau of Chem., Dept. of Agr., Washington, D. C.

Cook, A. D., 706 W. Green St., Urbana, Ill.

Dalton, N. N., 2451 Michigan Ave., Chicago.

Dean, John G., International Portland Cement Co., Toronto, Ontario.

Fell, J. William, 117 Chestnut St., Ashville, N. C.

Flintermann, R. F., 2627 No. Ashland Ave., Chicago.

Fox, H. W., U. S. R. & R. Co., Colorado Plant, Colorado Springs, Colo.

Grabfield, Joseph P., care of Jacob Grabfield, 238 Franklin St., Chicago, Ill.

Hall, Elmon L., 1613 Gough St., San Francisco, Cal.

Hartzell, L. J., 729 W. Quartz St., Butte, Mont.

Herty, Chas. H., care Bureau of Forestry, Washington, D. C.

Jackson, H. A., Columbia Univ., New York City.

Jefferson, (Miss) Alice M., to Mrs. Henri Guest Scott, The Pequot, 13th and Pine Sts., Philadelphia, Pa.

Jessup, Alfred E., care of U. S. Consul, Tientsin, China.

Johnson, Edward M., Cherokee Lanyon Spelter Co., Iola, Kans.

Johnson, G. A., Little Falls, N. J.

Jones, Arthur B., McKeesport, Pa.  
 Lamborn, L. L., 134 Willoughby Ave., Brooklyn, N. Y.  
 LeBosquet, M., 156 Tremont St., Boston, Mass.  
 Lustig, A. L., Box 827, Providence, R. I.  
 Perkins, T. S., 39 Garden Pl., Brooklyn, N. Y.  
 Pretzfeld, Charles J., Box 305, Niagara Falls, N. Y.  
 Richardson, Dr. C. H., Dartmouth Coll., Hanover, N. H.  
 Roberts, Alfred E., 81 Beach St., N. Y. City.  
 Schiedt, R. C., 1043 Wheatland Ave., Lancaster, Pa.  
 Schoonmaker, H., La Democrata de Cananea, Sonora, Mexico,  
 Apartado 28.  
 Smith, Francis P., 20-21 Queenhithe, London, E. C., England.  
 Stoddart, Chas. W., 246 Equitable Bldg., Denver, Colo.  
 Thayer, Harry S., Greeley, Colo.  
 Townsend, C. P., National Union Bldg., Washington, D. C.  
 Van Brunt, Charles, 124 E. 28th St., N. Y. City.  
 Young, E. H., Hartline, Wash.

## MEETINGS OF THE SECTIONS.

### NORTH EASTERN SECTION.

The regular meeting of the North Eastern Section of the American Chemical Society was held Saturday, November 29th, at Room 22, Walker Building, Massachusetts Institute of Technology.

Mr. Francis FitzGerald, of the International Graphite Company of Niagara Falls, addressed the Society on "The Acheson Furnace and Its Products," describing the processes and apparatus used by the company in the manufacture of carborundum and graphite.

The following officers for the ensuing year were elected:  
*President*—Augustus H. Gill; *Vice-President*—Henry Howard;  
*Secretary*—Arthur M. Comey; *Treasurer*—B. F. Davenport;  
*Executive Committee*—R. P. Williams, G. P. Baxter, B. S. Merigold, H. C. Lythgoe, Henry Fay; *Members of the Council*—H. P. Talbot, L. P. Kinnicutt, C. L. Parsons.

ARTHUR M. COMEY, *Secretary*.

### WASHINGTON SECTION.

The 137th regular meeting was called to order at 8.10 P.M., November 13, 1902.

The following program was presented :

H. Carrington Bolton, "A Chapter in the History of the Barometer."

F. K. Cameron and J. F. Breazeale, "The Estimation of Organic Matter in Soils."

The authors point out objections to the loss on ignition and humus methods, and conclude that it is safer to use a combustion method, even though it involves some arbitrary factor such as the well-known figure 0.471 proposed by von Bemmelen, Wolff, Wollny, and others. They have found that rapid and satisfactory combustions can be made in a moist way by mixing the dry soil with an equal weight of potassium bichromate, and then gradually adding pure water-free sulphuric acid. The mixture is then cautiously heated until the sulphuric acid begins to fume. The operation is carried on in an apparatus consisting of a flask with appropriate connections and a series of bulbs to catch the carbon dioxide generated. A current of air free from carbon dioxide is aspirated through the apparatus during the operation, and precautions are taken to prevent chlorine, hydrochloric acid, sulphur dioxide, etc., from reaching the potash bulbs, which are to be weighed. It was explained how this wet combustion method is free from objections which have been urged against similar procedures hitherto proposed, and experimental evidence was adduced to show that satisfactory results could be obtained when working with known organic compounds. Inherent difficulties in dry combustions, when working with *soils*, disappear in this wet combustion method as experimental evidence showed. The method is fairly rapid, two men working together in a day of seven hours averaging twelve to fourteen determinations.

L. S. MURSON, *Secretary*.



## Proceedings.

### MINUTES OF THE TWENTY-SEVENTH GENERAL MEETING OF THE AMERICAN CHEM- ICAL SOCIETY.

The twenty-seventh meeting of the American Chemical Society was held in the Medical School building of Columbian University, Washington, D. C., December 29 and 30, 1902. The first session was called to order by the president, at 11.45 A.M., Monday, December 29th.

The minutes of the previous meeting were adopted as recorded by the secretary.

The secretary read to the Society a letter from Sir Henry E. Roscoe, expressing regret at his inability to attend the meeting, and expressing also his high appreciation of the character and work of the American Chemical Society.

The secretary also exhibited a book on "Dalton's Atomic Theory" by Messrs. Roscoe and Harden, which Professor Roscoe had sent as a contribution to the library of the Society. The Society, through its president, instructed the secretary to send a suitable reply of appreciation and thanks to Professor Roscoe.

Dr. E. A. de Schweinitz, dean of the Medical School of Columbian University, addressed a few words of cordial welcome to the visiting chemists, and the regular program of papers was then taken up.

The first paper was by Dr. E. A. de Schweinitz, on "Some of the Work of the Bio-Chemic Division, Department of Agriculture." This paper was discussed by Messrs. Long and de Schweinitz.

The next paper was by A. H. Gill. Subject, "Does Cholesterol Occur in Corn Oil?" This was read by the author and followed by a paper on "Miley's Colour Photography", by W. G. Brown. The latter paper was discussed by Messrs. Baekeland, Brown, and Long.

The morning session of the Society was then adjourned.

In the afternoon the chemists visited the liquid air plant at the terminus of the Seventh Street Railway. In the evening, at the conclusion of the address of Professor Hall before the American Association for the Advancement of Science, the Council of the American Chemical Society met in the Columbian University Medical School.

#### TUESDAY, DECEMBER 30.

The meeting of the Society was called to order at 9.30 a. m. by the secretary, in the absence of the president, who was engaged in official duties as president of the American Association for the Advancement of Science. Vice-President H. A. Weber was called to the chair. The following papers were presented and discussed:

1. "The Composition of Fresh and Canned Pineapples," by L. S. Munson and L. M. Tolman.
2. "Chemical Composition of Some Tropical Fruits and Fruit Products," by E. M. Chace, L. S. Munson and L. M. Tolman.
3. "The Composition of Renovated or Process Butter," by C. A. Crampton.
4. "Nature of the Work of the Bureau of Chemistry, Department of Agriculture," by H. W. Wiley.
5. "The Composition of Spirits Produced from Grain, and the Changes Undergone by the Same when Stored in Wooden Packages," by C. A. Crampton.
6. "Iodine Absorption of Oils: Comparison of Methods," by L. M. Tolman and L. S. Munson.
7. "The Relation of the Specific Gravity of Urine to the Solids Present," by John H. Long.
8. "Derivatives of Isoapiol and Isosafrol," by F. J. Pond; read by title.
9. "Some Double Salts of Organic Acids," by James Lewis Howe.

At the conclusion of this part of the program, the annual reports of the secretary, treasurer and librarian were presented and ordered on file.

Dr. W. A. Noyes presented an oral report as editor, and also as chairman of the Committee on Papers and Publications.

President Remsen announced as a result of the annual election

that J. H. Long had been elected president of the Society for the year 1903, and the following named persons councillors, to serve three years beginning January 1, 1903: Messrs. Albert C. Hale, F. P. Venable, J. W. Richards, and L. P. Kinnicutt.

Dr. Hillebrand read the following communication and made some remarks upon the same:

Thorn Smith, chemist for the Ducktown Sulphur, Copper and Iron Company, Limited, of Isabella, Tennessee, sent out, a year ago, 40 samples of copper slag for a practically complete analysis. Analytical data were received from over 20 chemists in various parts of the world and these results, together with appropriate criticisms, will shortly appear in the *Engineering and Mining Journal*. Another review, prepared by Dr. Clifford Richardson, of Long Island City, New York, and Dr. W. F. Hillebrand, of the United States Geological Survey, will appear in an early issue of the *Journal of the Society of Chemical Industry*.

Mr. Smith started out with the idea that poor work is altogether too common, and a most cursory examination of the articles mentioned demonstrates it a fact. He will shortly send out another series, together with approved methods of analysis, and asks the cooperation of members of this Society. The work will be carried on as a part of the plan of the Committee on Uniformity in Technical Analysis of the New York Section of the Society of Chemical Industry.

Every member of this Society interested in advancing the cause of more accurate work in ordinary analysis is invited to correspond with Mr. Smith. He particularly desires the aid of college instructors.

THORN SMITH,  
Isabella, Tennessee.

December 27, 1902.

Upon motion of Professor Clarke, the communication read by Dr. Hillebrand was placed on file.

Dr. Hillebrand also made some announcements from the local committee.

It was voted that a committee of five be appointed to report upon the quality of the reagents furnished by dealers in this country, and that the committee consist of the president, as chair-

man, and four other members to be appointed by him. This committee as constituted consists of the following named gentlemen: J. H. Long, W. F. Hillebrand, H. P. Talbot, Charles Baskerville, and L. M. Dennis.

After some announcements the morning session was adjourned.

The afternoon session convened at two o'clock. The session was called to order by President Remsen, and the following papers were presented and discussed:

1. "Report of the Committee on Atomic Weights," by F. W. Clarke.
2. "Report of the International Committee on Atomic Weights," by F. W. Clarke.
3. "The Chemical Work of the Bureau of Soils, Department of Agriculture," by Frank K. Cameron.
4. "The Action of Metallic Magnesium on Aqueous Solutions," by Louis Kahlenberg. Discussed by Messrs. W. G. Brown, A. A. Noyes, Bancroft and Kahlenberg.
5. "Action upon Metals of Solutions of Hydrochloric Acid in Various Solvents," by Harrison E. Patten. Discussed by Messrs. Remsen, Patten, Kahlenberg and A. A. Noyes.
6. "A Proposed Method of Examining Wood Treated to Resist Fire," by C. F. McKenna.
7. "An Electric Test Retort," by C. F. McKenna.

On motion of the secretary, the thanks of the Society were voted to the Chemical Society of Washington; the local committee of arrangements, the governing board of the Cosmos Club; officers and faculty of Columbian University Medical School; Mr. Eugene C. Foster; the Heurich Brewing Company; Mr. Christian Heurich; Mr. William M. Meredith, director, and Mr. Thomas J. Sullivan, assistant director, of the United States Bureau of Printing and Engraving; and the *Brooklyn Daily Eagle*, for courtesies received and enjoyed by the Society.

After some announcements, the twenty-seventh general meeting of the Society was declared adjourned.

After the adjournment of the annual meeting, the Council of the Society met in Lecture Room No. 3 and elected the various officers and committees for the year 1903. Some other business was also transacted.

At 7:30 Tuesday evening the address of the retiring president, President Ira Remsen, was delivered in the large lecture room on

the first floor of the Columbian University Medical School. The subject of the address was "The Life History of a Doctrine". Professor F. W. Clarke presided.

At 9.00 P.M. the chemists enjoyed a subscription dinner at Hotel Barton. Dr. W. F. Hillebrand presided and President Remsen officiated as toast-master.

On Wednesday evening the chemists enjoyed a complimentary smoker tendered to them by the resident members of the Chemical Society of Washington. The smoker was held in the New Willard Hotel.

ALBERT C. HALE, *Secretary*.

#### REPORT OF THE SECRETARY FOR 1902.

The record of the American Chemical Society for the year 1902 contains many items of importance and shows some special changes in the administration of the Society. An index to the first twenty volumes of the Journal and to the earlier Proceedings has been printed; the twenty-fifth anniversary number has been published and distributed to the members; and the regular numbers of the Journal have been of special interest, and more voluminous than ever before. Besides the matter included in the Journal proper, the Review of American Chemical Research, in the hands of the large and able corps of abstractors who have worked assiduously and thoroughly in their respective fields, has received much more attention than formerly.

The membership of the Society has grown from 1,933, reported last year at the Philadelphia meeting, to 2,188 at the present time, a net gain of 255. With the exception of the years 1894 and 1898, this is the largest increase of membership in any single year in the history of the Society, and it was exceeded by only three persons in 1898 and only eight in 1894. The membership statistics at the present time are as follows:

Honorary members.....	15
Life members .....	13
Members .....	2160
<hr/>	
Total.....	2188
Elected but not qualified.....	80
Applications pending.....	14
<hr/>	
Grand total.....	2282

During the year the Society has lost by death the following

named members: Samuel S. Taite, Philadelphia; Charles Q. Rawling, Wheeling, West Virginia; Albert R. Leeds, Hoboken, New Jersey; Joseph Richards, Philadelphia; William S. Robinson, Omaha; R. F. Means, Boston; Henry Morton, Hoboken, New Jersey; G. C. Hubbard, New York City; James Hartford, New York City; George M. Richardson, Stanford University; W. Ivison Macadam, Edinburgh, Scotland; W. M. Mew, Washington; Edwin E. Hunter, St. Joseph, Missouri; Herbert S. Burgess, Providence; Robert C. Kedzie, Agricultural College, Michigan.

During the year one additional local section, the Cornell Section, with headquarters at Cornell University, Ithaca, New York, has been established. It was chartered December 9th, and held its meeting for organization December 15th. Professor L. M. Dennis is president of the section, and also its delegate to the Council of the Society. Members of the Society in three other localities have been in correspondence with the secretary in reference to the formation of local sections in their regions, and in one or two of these cases a formal application may be made before long for a local section charter. There are now fifteen local sections of the Society with membership as follows:

Rhode Island Section.....	33
New York Section.....	520
Cincinnati Section.....	60
Washington Section.....	137
Lehigh Valley Section.....	16
Chicago Section.....	104
Nebraska Section.....	17
Columbus Section.....	22
North Carolina Section.....	25
Northeastern Section.....	257
Philadelphia Section.....	145
Michigan Section.....	71
Kansas City Section.....	36
California Section.....	77
Cornell Section.....	32

Total number of members in local sections.....	1552
Per cent. of membership in local sections.....	71

Inasmuch as the constitution provides that these sections may draw from the treasury of the Society, for necessary current expenses, a sum equal to one-third of the total amount paid by their

members for dues during the current year, a considerable proportion of the gross receipts of the Society is thus rendered unavailable for defraying its regular expenses.

A large committee has been appointed by the president under the authority of the Council to enlist the interest of the chemists of this country in the Fifth International Congress of Applied Chemistry, which is to be held in Berlin early next summer. This committee is already at work vigorously, and it is to be hoped that the chemists of America will have their full share in the Congress and its work.

An invitation has been given to the members of the Society through the columns of its Journal to become co-laborers in the compilation of a trilingual technical dictionary to be issued in German, English, and French, and to be called the "Technolexicon." Several of the members have signified their desire to aid in this enterprise, which is undertaken by the Society of German Engineers.

Amendments to the constitution of the Society have been made this year by which the class of associates has been abolished, and any person interested in the promotion of chemistry may be elected to full membership in the Society. It is believed that this action will result in a considerable increase in membership, and that it will not detract from the high standard of work and influence which the Society has always striven to maintain.

The summer meeting this year was held in Pittsburg, Pennsylvania, June 30 and July 1, in connection with the meetings of Section C of the American Association for the Advancement of Science. The meeting was well attended, a large number of papers was presented, and matters of special interest were considered. The secretary, who has served the Society continuously since the year 1889, presented to the Council at this meeting a communication in which he announced that he would not be a candidate for re-election to the office he had held so many years. The Council subsequently voted "that the duties of the offices of secretary and editor be combined and that the same person be elected to serve in the two offices after the close of the present calendar year".

The annual meeting of the Society is held this winter, for the first time, in connection with the meeting of Section C of the

American Association for the Advancement of Science, that body having changed the date of its meeting to "Convocation Week," *i. e.*, the week in which January 1 occurs. If similar conditions are to prevail hereafter, it may be found desirable to seek a new arrangement with Section C, by which the American Chemical Society may have as much of the time of the meetings allotted to its use as it has heretofore had at its disposal when its annual meeting has been held alone.

This is the third general meeting that the Society has held in the city of Washington. Its first meeting here, which was the third general meeting held by the Society, occurred August 17 and 18, 1891, in connection with the meeting of the American Association for the Advancement of Science. The membership of the Society was then only 293, and there was only one local section. At this meeting there was a conference held by delegates sent by chemical societies from various sections of the United States to consider the best means for securing a permanent organization of chemists, which should be truly national in its character and aims. At this conference the American Chemical Society was accepted as such permanent representative body of American chemists and it was decided to carry into effect a plan of reorganization of the Society on such a basis that the desired results could be attained.

The second Washington meeting was held December 29 and 30, 1897, just five years ago. This was the sixteenth general meeting of the Society. Its membership was then 1,156, an increase since the first Washington meeting in 1891 of 863 members, and instead of one local section, as before, ten sections had been established. Since the second Washington meeting in 1897, the membership has increased 1,032, being now 2,188. There has also been an increase of five local sections during these five years, the total number at present being 15.

The city of Washington has furnished three of the twenty-one presidents who have administered the affairs of the Society; *viz.*, H. W. Wiley, during the years 1893 and 1894; C. E. Munroe in 1898; and F. W. Clarke in 1901. During Dr. Wiley's second term the increase in membership of the Society was the largest in its history, *viz.*, 263; and during Dr. Munroe's administration the next largest, 258. During Professor Clarke's administration the twenty-fifth anniversary meeting was held. During these four years of administration by Washington members of the Society,



there was a total increase in membership of 812, and a net increase of four local sections.

The present condition of the Society is very gratifying and its future looks very promising, but we are constrained to say that if the Society is to fill its proper sphere of usefulness in America and to exert the influence abroad which it should permanently hold, it behooves every member to be loyal and devoted to its interests and steadily to endeavor to insure its best development and growth. Any new departures like those inaugurated during the year just closing should be carefully tested and should be given every opportunity to demonstrate their value. Whatever is good should be retained and jealously guarded, and anything that is lacking should be promptly and fully supplied. It is perhaps now more important than ever before that the administration of the Society be wise, energetic, sufficiently conservative and yet continually aggressive and alive to every new demand that shall be made upon it. No phase of our science, whether pure or applied, theoretical or practical, should be ignored or in any way neglected. Every department of chemistry should be aided and inspired by the Society, and should be fully represented in its administration; all chemists in America should be loyal and enthusiastic members of the American Chemical Society, and should strive to keep it upon the highest plane which our science may be able to occupy, and to maintain it in the front rank of organizations established and administered in the interests of chemistry and those devoted to its advancement.

#### REPORT OF THE EDITOR.

During the year ending December 1, 1902, 179 papers have been submitted to the Committee on Papers and Publication. Of these, 127 have been accepted and have been or will be published; 21 have been accepted, after revision; 31 have been returned to the authors as being unsuited for publication in our Journal, and action upon one paper is still pending.

At the close of 1901 a new corps of reviewers was organized for the Review of American Chemical Research. The scope of the Review was also enlarged to include abstracts of work published abroad by American authors and to include abstracts of American patents. The number of pages in the Review given to each subject, during the year, are as follows:

	Pages.
General and Physical Chemistry.....	27.2
Inorganic Chemistry .....	12.6
Mineralogical and Geological Chemistry.....	76.7
Analytical Chemistry.....	12.8
Metallurgical Chemistry and Assaying.....	101.7
Organic Chemistry .....	47.6
Biological Chemistry.....	39.3
Pharmaceutical Chemistry.....	4.1
Sanitary Chemistry.....	45.8
Industrial Chemistry .....	33.2
Agricultural Chemistry .....	42.2
Patents .....	100.8

Total..... 544.0

W. A. NOYES.

REPORT OF THE TREASURER FROM DECEMBER 21, 1901, TO  
DECEMBER 21, 1902. \*

Balance on hand December 21, 1901.....\$ 1,957 31

RECEIPTS.

Received for dues .....	\$ 9750 00
“ “ advertising .....	1322 24
“ “ subscriptions .....	1110 79
“ “ back numbers and Index.....	415 05
“ “ interest Knickerbocker Trust Co.....	79 21
“ “ “ special investment fund .....	70 00
“ “ “ life membership fund .....	35 00
“ “ 25th anniversary fund.....	97 92
“ “ Michigan Section.....	44 38
“ “ circulars for general meeting.....	2 00
	<hr/> \$12,926 59
	<hr/> \$14,883 90

DISBURSEMENTS.

For printing Journal, 11 numbers .....	\$ 5945 00
“ “ “ anniversary number.....	459 05
“ authors' reprints .....	370 19
“ expense, president's office.....	35 38
“ “ editor's office (salary).....	500 00
“ “ “ “ (salary, abstract).....	150 00
“ “ “ “ (general) .....	121 42
“ “ secretary's office (clerical).....	602 23
“ “ “ “ (current).....	65 67
“ “ “ “ (general).....	274 85
“ “ “ “ (collection of dues).....	975 00
“ “ librarian's office .....	972 84
“ “ library, binding account, 1901.....	61 75

For expense, advertising.....	253 29
“ “ rebate on subscriptions.....	25 40
“ “ back numbers, storage, etc.....	66 60
“ “ printing directories.....	234 25
“ “ printing index.....	530 20
“ “ Review of American Chemical Research..	379 70
“ “ special appropriations.....	78 00
“ “ Membership Committee.....	5 52
“ “ general meetings.....	269 80
“ “ 25th anniversary.....	12 50
“ “ treasurer's office.....	400 00
“ “ incidentals.....	76 95
	<hr/>
“ “ local sections, viz:	\$12,875 59
Chicago.....	\$ 78 33
Cincinnati.....	46 66
Columbus.....	28 33
Kansas City.....	30 25
Michigan.....	83 33
Nebraska.....	30 00
New York.....	375 00
North Carolina.....	26 66
North Eastern.....	428 33
Philadelphia.....	50 95
Rhode Island.....	35 00
San Francisco.....	88 33
Washington.....	185 00
	<hr/>
	\$ 1486 17
Unpaid bills.....	14,361 76
	<hr/>
	535 85
Deposited in Emigrant Savings Bank.....	13,825 91
	<hr/>
	35 00
Bills of 1901.....	13,860 91
	<hr/>
	298 35
Balance on hand.....	14,159 26
	<hr/>
	724 64
	<hr/>
	\$14,883 90
ASSETS.	
Special investment fund (\$2000, 3½ per cent. N. Y. gold bond due 1915).....	\$2097 50
Life-membership fund (\$1000, 3½ per cent. N. Y. gold bond due 1925).....	\$ 1080 38
In Emigrant Savings bank.....	876 10
Interest from “ “.....	14 77
Interest from special investment bond.....	70 00
	<hr/>
	2041 25

<i>Amount brought forward</i> .....	2041 25
Balance in Knickerbocker Trust Co.....	724 64
Cash in secretary's hands.....	252 73
Uncollected accounts (advertising).....	850 00
"      "      (dues, 1901).....	440 00
"      "      ( " 1902).....	1130 00
	<u>\$ 7,536 12</u>

## LIABILITIES.

Life membership fund.....	\$1956 48
Unpaid bills.....	535 85
	<u>\$2492 33</u>
Balance of actual assets.....	5033 78
	<u>\$ 7,536 12</u>

A. P. HALLOCK, *Treasurer.*

## REPORT OF THE LIBRARIAN.

Copies of the Journal in stock December 20, 1901...	52,033
Copies received to December 20, 1902 :	
Journal .....	9,037
Index.....	2,931
Anniversary No.....	603
	<u>12,571</u>
	64,604
Copies sent out from December 20, 1901, to December 20, 1902 :	
To members and others without charge .....	3,725
By sale { Journal .....	807
{ Index .....	135
	<u>4,667</u>
In stock December 20, 1902 .....	59,937
Receipts from sale of Journal and Index from December 1, 1901 to December 20, 1902:	
Transmitted to treasurer.....	\$415.05
Balance in librarian's hands.....	40.11
	<u>\$455.16</u>

In my last report I called attention to the fact that there were six issues of the Journal of which we had less than 20 copies each. At present there are 7 such issues as follows :

Vol.	III,	No.	Aug.-Dec.	16 copies.
"	VI,	"	1 and 2	15 "
"	"	"	3	9 "
"	XVII,	"	10	17 "
"	XXII,	"	1	1 "
"	"	"	2	2 "
"	"	"	3	14 "

The two numbers of Vol. XXII, of which we have one and two copies, respectively, will probably be exhausted within a month or so. Of the other numbers the supply will probably be sufficient to meet the demand for several years.

#### EXPENSES OF THE LIBRARIAN'S OFFICE.

E. G. Love, librarian, in account with the American Chemical Society.

##### DR.

Dec. 1, 1901. To balance of appropriation.....	\$ 67.20
Dec. 1, 1901. To balance cash.....	10.73
Dec. 6, 1901. To A. P. Hallock, Treasurer.....	25.00
	<hr/> \$ 102.93

##### CR.

Dec. 30, 1901. By postage.....	5.07
Dec. 30, 1901. By express and incidentals.....	3.50
Feb. 26, 1902. By bill for binding (App. 1901) .....	61.75
Feb. 26, 1902. By balance of appropriation not drawn	5.45
	<hr/> 75.77
	<hr/> 27.16

Under appropriation of \$1000 for librarian's office for 1902.

##### DR.

Jan. 1, 1902. To balance.....	27.16
Jan. 20, 1902. To A. P. Hallock, Treasurer.....	250.00
Mar. 28, 1902. To A. P. Hallock, Treasurer.....	250.00
July 3, 1902. To A. P. Hallock, Treasurer.....	250.00
Oct. 10, 1902. To A. P. Hallock, Treasurer.....	222.84
	<hr/> 1000.00

##### CR.

January 1, 1902, to December 20, 1902:

By postage.....	140.72
By stationery and printing...	42.77
By clerical services and cataloguing.....	136.80
By completing files and binding.....	454.54
By express and incidentals .....	67.22
By storage at Chemists' Club.....	75.00
By subscriptions to journals.....	42.50
	<hr/> 959.55
Balance.....	<hr/> 40.45

The number of volumes bound since my last report, including those at the binders at the date of that report and paid for out of the appropriation for 1901, was 314, at a cost of \$314.90.

The librarian has purchased during the year to complete files 86 volumes and 284 single numbers.

E. G. LOVE, *Librarian.*

REPORT OF THE COMMITTEE ON EXCHANGES.

There are at present 82 exchanges on our list, of which 19 are weeklies, 42 semi-monthlies and monthlies, and 21 bi-monthlies, quarterlies and annuals.

During the year the following periodicals have been added to our exchange list:

Memoirs and Proceedings of the Manchester Literary and Philosophical Society.

Electrochemische Zeitschrift.

U. S. Geological Survey.

Royal Academy of Science, Amsterdam.

Archives des Sciences physiques et naturelles, Geneva.

Thonindustrie Zeitung.

Chemische Zeitschrift.

Revue de Chimie Industrielle.

The following have been dropped from our exchange list:

Bulletin New York Public Library.

Schuh und Leder.

The Sugar Beet.

Leipziger Farber Zeitung (for non-receipt).

There are many publications which it is important to have in the Society library, but which have no exchange list, or with which we have been unable so far to effect an exchange. Among these are the following which have been taken by subscription for the past few years.

London, Ed. and D. Philosophical Magazine.

Annales de Chimie et de Physique.

Chemiker Zeitung.

Dingler's polytechnisches Journal.

Berichte der deutschen chemischen Gessellschaft.

Zeitschrift für physikalische Chemie ( $\frac{1}{2}$ ).

It is hoped in the future to obtain the Berichte der deutschen chemischen Gessellschaft by exchange.

E. G. LOVE, *Chairman*.

REPORT OF COMMITTEE ON AMENDMENTS TO THE CONSTITUTION.

During the year important improvements to our constitution were made relating to the classification of our membership. These amendments do away with the class of members known as associates and classify all members of the Society into members, life

members, and honorary members. Members and life members have exactly the same standing in the Society. The life members differ from the other members only in paying at one time a sum which, it is estimated, will liquidate their dues as members.

Members in voting on important questions such as the amendments to the constitution have, apparently, shown lack of interest. Out of a membership of 2,200 in round numbers, only 446 voted on Amendment 1, which was the maximum voting on any of the amendments—almost exactly 20 per cent. When it is considered that the only trouble that the members would have in voting on these questions is to sign their names and transmit the ballot to the secretary, it seems strange that only 20 per cent. of the members took enough interest in the matter to record their ballots.

Your committee beg to submit the statement that while it is evident that the constitution of our Society is by no means perfect, yet under the conditions existing, we have continued to grow in a most phenomenal manner. The business of the Society is transacted with reasonable despatch and with reasonable expense, and it does not appear desirable at the present time to change any further the fundamental basis on which our Society rests. At least, not until a few years of experience has shown us, beyond a shadow of a doubt, the necessity for the proposed changes.

H. W. WILEY, *Chairman.*

#### REPORT OF THE COMMITTEE ON DUTY-FREE IMPORTATIONS.

Since the last report of this committee was presented at the Denver meeting of the Society, and published in the number of the Journal for January, 1902, there has been sent out from the office of the Secretary of the Treasury at Washington a circular of instructions to officers of the customs—Department Circular, No. 108, dated August 19, 1902—in which rules are laid down for the guidance of officials at the custom-houses of the United States in interpreting and administering the law in regard to duty-free importations by institutions of learning.

Unfortunately it cannot be said that these rules are altogether clear or free from ambiguity, nor do they seem to be entirely consistent with each other. It is evidently much to be desired, both with a view to the honest collection of government revenue and to the advancement of the scientific and educational interests of the United States, that a clearly intelligible, unambiguous and self-

consistent exposition of the law should be put forth by the Secretary of the Treasury. To secure such an exposition it seems desirable that a further effort be made to ask the attention of the Secretary to one or two points of general principle.

1. There does not appear to be any difficulty in regard to securing the duty-free admission of such articles or objects as are usable *solely* for scientific or educational purposes—for example, an apparatus for demonstrating the phenomena of optical diffraction.

2. It seems to be equally clear that articles are not entitled to exemption from payment of duty which, although they may be used by teachers or scientific investigators, are used by them for their personal comfort or convenience, and not as direct means for the advancement or diffusion of knowledge—for instance, the chair on which the teacher sits, or the cooler from which ice-water for drinking is supplied in the lecture-room.

3. The cases which have given rise to controversy are those in which articles or objects are concerned which are capable of being used for strictly scientific or educational purposes and also for the purposes of ordinary life—for personal convenience, or for gain and commercial advantage—as, for example, thermometers and filtering paper.

4. Sometimes an article of which the generic name would place it in the class of things used both for scientific and non-scientific purposes may be made of different types, some adapted only to use under one of these heads and some under the other. Thus we see 2-inch thermometers in ornamental frames on a parlor mantel-piece which would practically never be used for scientific teaching or research, and there are thermometers of precision, reading to hundredths of a degree, which would never be used for anything else than such teaching or research.

5. There remain, however, very many articles of which the fitness for either scientific or non-scientific use has led to disputes with custom-house officials in regard to exemption or non-exemption from duty, and it is especially under this head that a clear and easily understood rule is desirable.

6. In speaking of apparatus, materials, etc., as “used for scientific purposes” not only should the distinction be kept in view between such things being *capable* of such use and *being* so used, but also the distinction between their being *commonly* or *habitually*



*ally* so used in the world at large and their being *actually* so used by the particular universities, colleges, etc., importing them free of duty.

7. Having in view the spirit and reason of the law to be interpreted it would seem that the decision in doubtful cases should be based, not on the use to which the article in question is *capable* of being put or *may* be put, but on that to which it *actually is* put by the institution of learning seeking exemption from payment of duty. The applications for free entry at a custom-house are made under oath, by a class of men who have moral characters to sustain before the world, and whose personal interests are either not at all or only very indirectly concerned, and the law provides adequate punishment for falsehood in the statements embodied in such applications. If the present form of application were modified by inserting, after the statement that the articles imported are for the exclusive use of the institution of learning, some such words as —“to be applied directly and solely in teaching or in scientific investigation”—it seems that the interests of the Treasury would be safeguarded, and at the same time the facilities and advantages would be secured which the statute was intended to give to the intellectual life and progress of the country.

8. The general principle here advocated is supported by the last section (11) of the Treasury Circular No. 108, which reads thus: “In determining whether articles imported by colleges, etc., are entitled to free entry as being philosophical or scientific in character, the principal use of the article should be taken into consideration; and while an instrument may be used in the industrial pursuits, if its construction is based upon scientific principles and the article is used in the class-room in scientific teachings, it is clearly entitled to free entry. Sextants, quadrants, theodolites, calculating machines, etc., are illustrations of this class of instruments.” Unfortunately the language of this section seems to be in some measure contradicted by that of other sections of the circular.

9. It seems likely that more success might attend an effort to place this matter before the Secretary of the Treasury orally than by any lengthy memorial in writing, and it is recommended to the Society that a committee be authorized to seek a personal interview with the Secretary, and to present to him a statement of the difficulties sought to be overcome, and of the means by which they

may be surmounted without loss or injury to the government.

The committee in question, either that now in existence or a new one, might be given discretion as to the presentation to be made, or might be instructed by the Society after a general discussion of the subject.

Respectively submitted,

J. W. MALLET.

### COUNCIL.

The Council of the American Chemical Society met in the Medical School building of Columbian University, Washington, D. C., Monday, December 29, 1902. The meeting was called to order at 9.00 P.M. There were present Messrs. Remsen, Smith, Venable, Clarke, Talbot, Jennings, McPherson, A. A. Noyes, Dennis, Baskerville, Prescott, W. A. Noyes, Mallet, Catlin, Long, Munroe, Hale, Hallock, Parker, McMurtrie, Baekeland, Hillebrand, Marshall, and Stokes.

The minutes of the previous meeting were adopted as recorded by the secretary. The secretary read a report of the Committee on Exchanges, and it was ordered on file.

Dr. Munroe, chairman of the Committee on Duty-free Importations, read a report for that committee which was prepared by Dr. Mallet. It was voted that the report of the Committee on Duty-free Importations be accepted and adopted, and that a committee to confer with the Secretary of the Treasury be appointed by the president in conference with the members of the committee present. The president appointed as such committee of conference the members of the Committee on Duty-free Importations who were present. It was also voted that the Committee on Duty-free Importations be requested to obtain, if possible, concerted action by the various educational institutions throughout the country looking to such restatement of the law governing duty-free importations as will admit free of duty such apparatus and supplies as are imported in good faith by these institutions for instruction and investigation and are not intended for sale.

The Committee on Coöperation with the National Bureau of Standards reported progress through Dr. A. A. Noyes.

A report of the Committee on Amendments was read by the secretary and adopted by the Council. The committee was discharged.

The following named committees having completed their work, were also discharged: Committee on Administration, Committee on Twenty-Fifth Anniversary Volume, and the Committees on Program for the Twenty-Sixth and Twenty-Seventh Meetings.

The president and secretary were authorized to prepare and issue credentials to all members of the Society who shall attend the Fifth International Congress of Applied Chemistry in Berlin, accrediting them as delegates from the American Chemical Society. Upon motion of Professor Clarke, seconded by Dr. Hale, it was voted that hereafter the representatives of the American Chemical Society in the Council of the American Association for the Advancement of Science shall be the president and secretary of the Society, *ex officio*.

The following communication from the New York Section of the Society, sent to the Board of Directors, was read by the secretary, since action thereon comes properly within the province of the Council.

"NEW YORK, October 31, 1902.

"Mr. Albert C. Hale,

"Secretary American Chemical Society.

"DEAR SIR:

"At the regular meeting of the New York Section held October 10, 1902, it was voted that the New York Section recommend to the Board of Directors of the American Chemical Society that a photo reproduction of the Nichols medal be made and published in the Journal of the Society, and that it be accompanied with a statement of the conditions governing the award of the same.

"Yours truly,

"FRANCIS D. DODGE,

"Secretary New York Section."

The request of the Section was granted and it was ordered that such photo reproduction and description be inserted in the Journal.

The Committee on Resolutions Regarding the Retirement of the Secretary made the following report, which was adopted:

"The announcement of Dr. Albert C. Hale that he felt constrained to retire from active duty as secretary of the Society at this time came as a great surprise to those of us who have known of his splendid work and his deep and constant interest in the Society's progress and advancement. Having served by his side

in the "day of small things," and having observed his untiring efforts in every direction for the upbuilding of the Society and its recognition as a potent factor in the world of pure and applied science, the undersigned would take occasion to offer this minute of their appreciation, and the great regret which we all entertain in regard to his action, and to assure Dr. Hale that the sincere thanks of every member of the Society are his, not only for his accurate, competent, and careful discharge of the onerous, and at times trying and delicate, duties which devolved upon him as an official, but also for the frequent assistance and uniform kindness and courtesies of which we all have been the recipients from his hands. We beg to remind him that the place which he holds in our affections will not be made vacant, nor will his labors in our behalf be forgotten.

"EDGAR F. SMITH,  
 "CHARLES B. DUDLEY,  
 "WILLIAM McMURTRIE."

It was voted that the issue of the Journal be 3200 copies during the months of January, February, and March, 1903, and 3000 copies the balance of the year.

The president and secretary were appointed a committee with power to act in the matter of printing the constitution.

The report of the Committee on Estimates was submitted. Pending action thereon, the Council voted that the dues of the Society be collected by the treasurer.

It was moved that the secretary be given a salary of \$300 for the year and the treasurer a salary of like amount. This motion was amended to make the sum which each should receive \$250. The amendment was carried and the original motion as amended was adopted.

The following budget of expenses for the year 1903 was then adopted:

Journal and abstracts.....	\$6,475
Authors' reprints.....	350
Editor's office:	
Editor's salary.....	\$500
Abstract editor's salary.....	150
Abstract fees.....	500
Expenses of editor and abstract editor.....	200
	— 1,350

**Secretary's office:**

Secretary's salary .....	250
Clerk or stenographer for secretary.....	500
General expenses of secretary's office.....	350
Directory .....	250
	<hr/> 1,350

**Treasurer's office:**

Treasurer's salary.....	250
Expenses of treasurer's office.....	400
	<hr/> 650

**Librarian's office:**

Clerical.....	150
Postage, stationery and incidentals.....	260
Storage of journals at Chemists' Club.....	75
Subscriptions.....	45
Binding and completing files.....	500
	<hr/> 1,030

**Committees:**

Membership Committee.....	50
Committee on Advertisement.....	50
Committee on Atomic Weights.....	2
Other committees .....	23
	<hr/> 125

General meetings.....	250
Local sections.....	1,800
Special appropriations and contingent fund.....	500

Total..... \$13,880

The following estimate of receipts of the Society for the year 1903, which was reported by the Committee on Estimates, was accepted by the Council:

Membership dues.....	\$11,000
Subscriptions.....	1,100
Advertising .....	2,000
Sale of Journal and index.....	500
Interest.....	200
Balance on hand from 1902.....	250
	<hr/>
Total.....	\$15,050

The following were nominated as officers and members of committees, respectively for the year 1903:

*Secretary and Editor.*—W. A. Noyes.

*Treasurer.*—A. P. Hallock.

*Librarian.*—E. G. Love.

*Directors* (to serve two years beginning January 1, 1903).—C. A. Doremus, C. B. Dudley.

*Committee on Papers and Publications*.—W. A. Noyes, Edward Hart, W. F. Hillebrand, J. H. Long, William McMurtrie, A. A. Noyes, Edgar F. Smith, H. N. Stokes, H. P. Talbot, H. W. Wiley.

*Finance Committee*.—J. H. Wainwright, Durand Woodman, Charles F. McKenna.

*Committee on Membership*.—William McMurtrie, E. G. Love, C. L. Reese.

The retiring secretary was authorized to have bound the lists of members which he has been collecting for the Society. He was also authorized to incur all necessary expenditures in the transfer of the office and business of the secretary.

The president was instructed to appoint a committee to report at the meeting of the Council December 30th, on the time and place for the next meeting of the Society. He appointed as such committee J. H. Long and W. A. Noyes.

The matter of printing back numbers of the Journal was left to the president and secretary with power.

The Council then adjourned, to meet at the close of the annual meeting of the Society. ALBERT C. HALE, *Secretary*.

#### ADJOURNED MEETING OF THE COUNCIL.

The adjourned meeting of the Council was called to order in the Columbian University Medical School building at 4.15 p. m., December 30, 1902. The following named councillors were present: Messrs. Remsen, McMurtrie, Baekeland, Munroe, Dennis, Hale, Marshall, Catlin, Baskerville, Clarke, Talbot, A. A. Noyes, W. A. Noyes, Long, Smith, McKenna, Hillebrand, and Hallock.

The outline of minutes of the meeting of December 29th was read by the secretary and approved.

The Committee on Time and Place for the Next Meeting of the Society recommended Cleveland, Ohio, as the place, and June 30th and July 1st as the date. It was voted that Cleveland be accepted as the place of meeting, and that the exact date be left to the president and secretary to determine.

The report of the Committee on Patents and Related Legislation was read by P. T. Austen and adopted.

The secretary was instructed to cast the ballot of the Council, electing to the various offices and membership of committees the persons who were nominated for the respective positions at the meeting December 29th. The secretary cast the ballot and the gentlemen were declared elected.

Dr. Baekeland moved that the Council take action with reference to the bill upon the metric system now pending in Congress. The motion was seconded and the whole question was referred to the Committee on Coöperation with the Bureau of Standards.

The editor was empowered to vary, at his discretion, the size of the individual numbers of the Journal, providing the total issue during the year is kept within the authorized limits of expenditure.

The thanks of the Council were voted to Dr. Morley and Dr. Tower for their services in preparing the index of the Proceedings and first twenty volumes of the Journal. It was also voted that they be furnished gratis with such copies of the index as they may wish for their personal use, and that Dr. Morley be asked to retain for himself the set of the Journal and Proceedings which was used in their work.

The librarian was instructed to furnish to the chairman of the Committee on Advertising such copies of the Journal as may be needed in conducting the work of the committee. The librarian was also instructed to replace such numbers of the Journal as the chairman of the Committee on Advertising has withdrawn from his personal file to use in his committee work.

The Council then adjourned.

ALBERT C. HALE, *Secretary*.

#### INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS.

The following chemists have agreed to use the methods adopted by the Commission and printed in this Journal, 23, (1901)

##### UNITED STATES OF NORTH AMERICA.

1. Aldrich, Thos. B., Care Parke Davis & Co., Detroit, Mich.
2. Atkinson, J. W., Betteravia, Cal.
3. Babington, Fred. W., Chemist, Customs Dept., Ottawa, Canada.
4. Baum, Simon, Saint Rose P. O., Louisiana.
5. Behr, Arno, Pasadena, Cal.
6. Bennett, A. A., Ames, Ia.
7. Bennett, J. W., Boston, Mass.

8. Bentley, Wm. B., Ohio University, Athens, O.
9. Bevier, Isabel, University of Illinois, Urbana, Ill.
10. Bird, Maurice, Calhoun, La.
11. Bragg, Charlotte A., Wellesley, Mass.
12. Bryan, A. Hugh, Chemist, American Beet Sugar Co., Rockyford, Col.
13. Burr, E. C., San Francisco, Cal.
14. Cady, W. B., Care Bay City Sugar Co., Bay City, Mich.
15. Caldwell, George Chapman, Ithaca, N. Y.
16. Cavanaugh, Geo. W., Ithaca, N. Y.
17. Chamberlin, G. M., Jr., Bay City Sugar Co., Bay City, Mich.
18. Chamot, E. M., Ithaca, N. Y.
19. Chandler, Charles F., Columbia University, New York, N. Y.
20. Clapp, Lowell T., Boston, Mass.
21. Coates, Charles E., Louisiana State University, Baton Rouge, La.
22. Colby, George Elden, University of California, Berkeley, Cal.
23. Comey, Arthur M., 32 Hawley street, Boston, Mass.
24. Curtis, Henry E., Agricultural Experiment Station, Lexington, Ky.
25. Davidson, R. J., Blacksburg, Va.
26. Davoll, David L., Chemist, Pennsylvania Sugar Refining Co., Caro, Mich.
27. De Coninck, Frank, 102 Ellis street, San Francisco, Cal.
28. Dennis, Louis Munroe, Ithaca, N. Y.
29. Diehl, O. C., Detroit, Mich.
30. Doolittle, R. E., Lansing, Mich.
31. Dudley, Wm. L., Nashville, Tenn.
32. Eccles, R. G., Brooklyn, N. Y.
33. Eckart, Charles F., Honolulu, Hawaii.
34. Eddy, W. C., Norfolk, Nebraska.
35. Ehlert, T. G., Rochester, Mich.
36. Fields, John, Stillwater, Oklahoma.
37. Fitzmaurice, Charles Richard, State University, Reno, Nevada.
38. Fraps, G. S., Raleigh, N. C.
39. Frear, Wm., State College, Penn.
40. Fuller, F. D., Geneva, N. Y.
41. Getz, Wm. H., 1141 Market street, St. Louis, Mo.
42. Glenk, Robert, Audubon Park, New Orleans, La.
43. Goessmann, C. A., Amherst, Mass.
44. Goss, Arthur, Mesilla Park, New Mexico.
45. Gough, T. R., College Park, Md.
46. Graham, R. O., Bloomington, Ill.
47. Hare, R. F., Mesilla Park, New Mexico.
48. Harrington, H. H., College Station, Texas.
49. Harris, Isaac F., New Haven, Conn.
50. Harrison, J. B., Government Analyst, Georgetown, Demerara, British Guiana.
51. Haskins, Henri D., Amherst, Mass.
52. Hawk, P. B., New York, N. Y.



53. Heileman,<sup>1</sup> W. H., Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.
54. Hendelson, Hans, Great Western Sugar Co., West Bay City, Mich.
55. Herlitschka, Gustave, West Bay City Sugar Co., West Bay City, Mich.
56. Herty, Chas. H., Athens, Georgia.
57. Hibbard, P. L. Waukegan, Ill.
58. Hills, Joseph L., Burlington, Vt.
59. Hiltner, R. S., Lincoln, Nebraska.
60. Holland, Edward B., Amherst, Mass.
61. Hopkins, Cyril G., Urbana, Ill.
62. Horne,<sup>2</sup> W. D., Yonkers, N. Y.
63. Howard, S. Francis, Massachusetts Agricultural College, Amherst, Mass.
64. Hurty, J. N., Indianapolis, Ind.
65. Huston, H. A., Lafayette, Ind.
66. Hutchings,<sup>3</sup> R. J., Chemist, Utah Sugar Co., Lehi, Utah.
67. Hymer, Otis, Lincoln, Nebraska.
68. Jaffa, M. E., University of California, Berkeley, Cal.
- 69.\*Kedzie, R. C., Agricultural College, Mich.
70. Kedzie, Frank S., Lansing, Mich.
71. Kinnicutt, Leonard P., Polytechnic Institute, Worcester, Mass.
72. Knight, O. W., Bangor, Maine.
73. Knisely, A. L., Corvallis, Oregon.
74. La Bach, J. O., Agricultural Experiment Station, Lexington, Ky.
75. Ladd, E. F., Agricultural College, North Dakota.
76. Lawson, William, Alameda Sugar Co., Alvarado, Cal.
77. Lazell, E. W., 1110 Stephen Girard Building, Philadelphia, Pa.
78. Little, A. D., Little & Walker, Boston, Mass.
79. Long, J. H., 2421 Dearborn St., Chicago, Ill.
80. Lyon, T. L., Station A., Lincoln, Nebraska.
81. Love, E. G., New York, N. Y.
82. Macfarlane, Thomas, Ottawa, Canada.
83. Magruder, E. W., Department of Agriculture, Richmond, Va.
84. Marshall, John, University of Pennsylvania, Philadelphia, Pa.
85. Masser, A. M., Los Alamitos, Cal.
86. McIlhiney, Parker C., 145 E. 23rd St., New York, N. Y.
87. McDowell, M. S., State College, Pa.
88. McFarland, T. D., Marine City, Mich.
89. McKellips, C. M., Agricultural Experiment Station, Corvallis, Oregon.
90. McMurtrie, Wm., 444 West End Ave., New York, N. Y.
91. Mitchell, A. S., Milwaukee, Wis.
92. Momo Cuadrad, Dr. Gaston, Havana, Cuba.
93. Mooers, Charles A., Knoxville, Tenn.
94. Morse, Fred. W., Durham, N. H.
95. Morton, Henry, Stevens Institute of Technology, Hoboken, N. J.
96. Mudge, Charles W., Agricultural Experiment Station, Geneva, N. Y.

\* Deceased.

97. Nicholson, H. H., Lincoln, Nebraska.
98. Patterson, H. J., Agricultural Experiment Station, College Park, Md.
99. Pearce, J. A., Watsonville, Cal.
100. Peratta, Arthur A., Benton Harbor, Mich.
101. Perkins, W. R., Agricultural College, Miss.
102. Peter, Alfred M., Agricultural Experiment Station, Lexington, Ky.
103. Peters, Charles A., University of Idaho, Moscow, Idaho.
104. Pety, Henry, 180 Hawley St., Binghamton, N. Y.
105. Pond, G. G., State College, Pa.
106. Prescott, Albert B., Ann Arbor, Mich.
107. Price, T. M., College Park, Md.
108. Purenton, D. B., W. Va. University, Morgantown, W. Va.
109. Redding, R. J., Agricultural Experiment Station, Experiment, Ga.
110. Richards, Edgar, 341 West 88th St., New York, N. Y.
111. Richardson, Clifford, Long Island City, N. Y.
112. Robb, J. Bernard, College Park, Md.
113. Rogers, Allen, 3605 Locust St., Philadelphia, Pa.
114. Sabin, A. H., Long Island City, N. Y.
115. Schwarz, Dr. H. P., American Beet Sugar Co., Rockyford, Col.
116. Scovell, W. H., Agricultural Experiment Station, Lexington, Ky.
117. Sharples, S. P., Boston, Mass.
118. Shaw, G. W., Berkeley, Cal.
119. Shepard, Jas. H., Brookings, South Dakota.
120. Shutt, Frank T., Dominion Experiment Farms, Ottawa, Canada.
121. Skinner, W. W., Tucson, Arizona.
122. Smith, E. E., 26 E. 29th St., New York, N. Y.
123. Smith, Bernard H., Woodbine, N. J.
124. Smith, L. H., Agricultural Experiment Station, Urbana, Ill.
125. Spencer, G. L., U. S. Department of Agriculture, Washington, D. C.
126. Springer, Alfred, 312 East 2nd St., Cincinnati, Ohio.
127. Stebbins, James H., Jr., New York, N. Y.
128. Straughn, M. N., College Park, Md.
129. Struthers, D. H., Kalamazoo Beet Sugar Co., Kalamazoo, Mich.
130. Stubbs, Wm. C., Sugar Experiment Station, Audubon Park, New Orleans, La.
131. Stuhr, L. B., American Beet Sugar, Co., Rockyford, Col.
132. Test, W. H., Lafayette, Ind.
133. Thatcher, R. W., Pullman, Wash.
134. Thompson, John, Greensboro, North Carolina.
135. Torrey, Henry A., Burlington, Vermont.
136. Traphagen, F. W., Bozeman, Montana.
137. Treskow, F., Crockett, Cal.
138. Trowbridge, P. F., Ann Arbor, Mich.
139. Tucker, Willis G., Albany, N. Y. (Albany Medical College).
140. Tuttle, F. E., State College, Pa.
141. Ulmer,\* George F., Arbuckle Brothers, Brooklyn, N. Y.
142. Van Slyke, L. L., Agricultural Experiment Station, Geneva, N. Y.

143. Veenhuyzen, American Beet Sugar Co., Oxnard, Cal.
144. Vinson, Albert E., Columbus, Ohio.
145. Voorhees, E. B., New Brunswick, N. J.
146. Vulté, Hermann T., Teachers' College, Columbia University, New York, N. Y.
147. Wainwright, John W., 122 Hudson St., New York, N. Y.
148. Waller, Elwyn, 159 Front St., New York, N. Y.
149. Weber, H. A., Columbus, Ohio.
150. Weems, J. B., Ames, Iowa.
151. Welt, Dr. Ida, 128 East 61st St., New York, N. Y.
152. Wesson, D., Savannah, Georgia.
153. Weston, David B., Lansing Mich.
154. Wheeler, H. J., Kingston, R. I.
155. Whitehill, A. R., Morgantown, W. Va.
156. Wiley, Samuel W., Amherst, Mass.
157. Wiley, H. W., U. S. Department of Agriculture, Washington, D. C.
158. Willard, J. T., Agricultural Experiment Station, Manhattan, Kansas.
159. Wilson, Nathaniel E., Agricultural Experiment Station, Reno, Nevada.
160. Winton, A. L., New Haven, Conn.
161. Witthaus, R. A., First Avenue and 28th St., New York, N. Y.
162. Wolfe, W. W., Lyons, New York.
163. Woll, F. W., Madison, Wis.
164. Woodman, Durand, New York, N. Y.
165. Woods, Charles D., Agricultural Experiment Station, Orono, Maine.
166. Wrampelmeier, T. J., 328 Montgomery St., San Francisco, Cal.
167. Wyatt, Francis, National Brewers' Academy, 39 S. William St., New York, N. Y.

*Comments Made by Adhesionists who Signed with a Reservation.*

1. Heileman, W. H. In No. 8 of the resolutions I should like to have seen mercuric nitrate retained as a clarifying reagent. My experience with milk analysis (milk-sugar) proves this reagent to be almost indispensable on some samples.

2. Horne, W. D. In giving my adhesion to the proposed new regulations for polarizing sugars, I wish to suggest a modification of clause 6. Instead of taking the so-called mean of several independent readings I prefer to prove the correctness of one reading by the following method. I make my reading as close as possible and then I set the instrument  $0.2^{\circ}$  higher and look at the field which should now appear appreciably too high. Then I set the scale  $0.2^{\circ}$  below the supposed correct point and read again. The field should now appear appreciably too low and further it should appear just as much too low as the preceding reading seemed too high. I find this both practicable and safe, having employed it for several years in all my readings and in my assistants' work. It is more accurate than averaging readings for a man might always be 0.1 out on the average if his readings happened to all fall 0.1 high or all 0.1 low, but by my method if he is 0.1 too high at first his second reading will

put him 0.3 too high and his third reading only 0.1 too low, a discrepancy which is easily observed. He then knows his first reading to be incorrect and can try a reading 0.1 lower, with its suitable checks above and below.

3. Hutchings, R. J. I have thoroughly examined your circular gotten up by the International Committee for Unifying Methods of Sugar Analysis and they are very satisfactory to us with the exceptions of the first and second paragraphs; our water being 14° to 15° C. we could not adopt the 20° C.

4. Ulmer, Geo. F. While I favor all the rules adopted by the International Committee for the Unification of Sugar Analysis at the present time I could hardly agree to the first and second articles inasmuch as my polariscopes are graduated at 17.5° C., and there is considerable variation in the temperature of the laboratory.

#### BELGIUM.

1. Delville, Eduard, rue de Monnel 12, Tournai.
2. Desmurs, Jules, rue Suderman 22, Anvers.
3. Hanuise, Edouard, rue Hotel des Monnaies 54, Saint Gilles.
4. Lembourg, Edouard, a Quiévrain.
5. van Melckebeke, Ed., Aven. des Arts 22, Anvers.
6. de Puydt, Julien, rue de la Constitution 76, Anvers.
7. Sachs, François, rue d'Allemagne 63, Bruxelles.
8. Xhoneux, Pierre, Docteur en Sciences, Anderlecht, rue Wayez 170.

#### BRITISH GUIANA.

1. Vonziegesar, H. K. L., Analytical Chemist and Sugar Manufacturer, Georgetown, Waterloo Street 157.

#### GERMANY.

1. Ahrens, Dr. C., Inhaber Dr. Gilbert's Oeffentl. chem. Laboratorium, Hamburg. Deichstr. 2.
2. Alberti & Hempel, Hamburg. (Dr. Herrmann.)
3. Alberti & Hempel, Magdeburg. (Dr. Peters, Dr. Lühe.)
4. Brinkmann, Dr., Danzig, Hundegasse 109.
5. Creydt, Dr. Robert, Magdeburg.
6. Drenckmann, Dr. Bruno, Halle a. S.
7. Eckleben, Selmar, Danzig.
8. Frühling, Dr. R. and Dr. Julius Schulz, Inh. Prof. Dr. Frühling und Dr. Adalb. Rossing, Magdeburg.
9. Götting, Dr. Gustav, Breslau.
10. Haegele, Dr. E., Danzig, Hundegasse 51.
11. Hans, Wilh., Danzig, Hundegasse 109.
12. Heyer, Prof. Dr. Carl, Dessau.
13. Herzfeld, Prof. Dr. A., Berlin N., Invalidenstrasse 42.
14. Komoll, Dr. E., Magdeburg.
15. Köppen, Dr. O., beedigter Handelschemiker, Hamburg, Neue Gröningerstr. 4.
16. Kossak, Dr., i. F. Dr. Brockhoff & Ehrecke, Magdeburg.

17. Langfurth, Dr. Ad., Altona.
18. Marzahn, R., i. F. Dr. Heyer, Dessau.
19. Pieper, Dr. Oscar, Hamburg, Neue Gröningerstrasse 4.
20. Schulz, Dr. Julius, Magdeburg, i. F. Oeffentl. chem. Laboratorium Dr. Hugo Schulz.
21. Stegelitz, Dr. Paul, staatl. qual. Nahrungsmittelchemiker, Magdeburg, Fürstenwallstr. 15.
22. Thiele, Dr. A., Magdeburg, i. F. Dr. Rudolph Müller's Handelslaboratorium.
23. Weiss, Dr. G., beeidigter Handelschemiker, Hamburg, Brandswiete 46.
24. Wendel, Dr. Otto, Magdeburg, i. F. Oeffentl. chem. Laboratorium Dr. Hugo Schulz.
25. Woy, Dr. Rudolf, Breslau.
26. Friedrich, Dr. Ottomar, i. F. Dr. Friedrich and Dr. Rossée, Braunschweig.
27. Rossée, Dr. Willy, i. F. Dr. Friedrich and Dr. Rossée, Braunschweig, Turnierstr. 2.

## ENGLAND.

1. Biggart, J. W., (Messrs. McCowan & Biggart, Official Chemists to the Beetroot Association).
2. Fairrie, Henry, (Messrs. Fairrie & Co. Ltd.).
3. Macdonald, J. W., (Messrs. Henry Tate & Sons, Ltd.).
4. Stein, Sigmund, (Messrs. Crosfield, Barrow & Co.).
5. Thompson, W., (Messrs. The Sankey Sugar Co.).
6. Watt, Alexander, (Messrs. Macfie & Sons).

The chemists here named, at a meeting held March 8, 1901, agreed to use the methods of the commission with the reservation that when invert sugar does not exceed 0.25 per cent. it is to be determined volumetrically.

## HOLLAND.

1. Brunings, C. L., Scheikundige Suikerfabriek, "Holland", te Halfweg oy Haarlem.
2. Ekenstein, van, W., Alberda, Amsterdam.
3. Goossens, A., Scheikundige, Zevenbergen.
4. Ketel, van, B. A., Scheikundige, Amsterdam,, Brouwersgracht 56.
5. Leeuwen, Docters J. van, Amsterdam, Nicolaas Witsenstraat 1.
6. Loon, van, Dr. J., Technoloog. Steenberg.
7. Roos, van Hamel, Dr. P. F., Adviseur voor scheikundige en hygienische Zaken van het huis van H. M. de Koningin, Amsterdam, Keizersgracht 291.
8. Sleen, van der, N., Scheikundige, Haarlem, Oude-gracht 47.

## AUSTRIA-HUNGARY.

1. Barta, Gustav, Prag.
2. Bernheimer, Dr. Oscar, Wien.
3. Blumenfeld, Dr. J., Brünn.
4. Boschtschik, C., Brünn.

5. Dafert, Dr. F. W., Director der K. K. landw. chem. Versuchsstation, Wien.
6. Fallada, O., Wien.
7. Friedrich, Dr. H., Prag.
8. Graeger, F., Prag.
9. Herles, Franz, Prag.
10. Hodek, J., Prag.
11. Jettmar, J., Königgrätz.
12. Jolles, Dr. Ad., Wien.
13. Klaudy, Josef, Prag.
14. Koblic, Josef, Prag.
15. Kruis, J., Prag.
16. Kucera, F. L., Prag.
17. Liebermann, Prof. Dr. L., Director d. kgl. ungar. chem. Staatsversuchsanstalt in Budapest.
18. Mansfeld, Dr. M., Wien.
19. Neumann, K. C., Prag.
20. Neumann, Dr. S., Budapest.
21. Nevole, Dr. M., Prag.
22. Poledne, Joh., Prag.
23. Schiff, Dr. Felix, Wien.
24. Stein, A., Prag.
25. Stift, A., Wien.
26. Strohmer, F., K. K. Regierungsrath, Director der Versuchsstation des Centralvereins für Rübenzuckerindustrie in Wien.
27. Szilasi, Dr., & Bernauer, Budapest.
28. Telbisz, Dr. Joh., Budapest.
29. Völker, Dr. O., Kolin.
30. Weinwurm, S., Wien.
31. Weiss, J. J., Prag.
32. Willigk, Th., Prag.

NEW MEMBERS ELECTED BETWEEN DECEMBER 26, 1902, AND JAN-  
UARY 24, 1903.

- Apfel, Philip F., 107 N. 51st Court, Chicago, Ill.  
 Arnold, Edward E., 55 Canal St., Providence, R. I.  
 Baur, H. F., 1351 E. Sunnyside Ave., Chicago, Ill.  
 Brenke, G. A., 75 Wells St., Chicago, Ill.  
 Bryant, George O., Saylesville, R. I.  
 Capen, George H., Canton Junction, Mass.  
 Cappell, Walter, 238 Gilman Ave., Cincinnati, O.  
 Carroll, Charles Geiger, Georgetown, Texas.  
 Cary-Curr, Henry J., 143 E. Lake St., Chicago, Ill.  
 Clarke, Charles H., Grace Mine, Ont., via Michipicoten River.

- Cottrell, F. G., University of California, Berkeley, Cal.  
 Dodd, Louis C., Snow Steam Pump Works, Buffalo, N. Y.  
 Du Pont, Francis I., Wilmington, Del.  
 Durkee, Myron Clark, 386 Bergen Ave., Jersey City, N. J.  
 Fairchild, B. F., 56 Laigle St., New York, N. Y.  
 Farnan, Earl Frederic, 26 Grand Ave., Chicago, Ill.  
 Farrington, Charles E., 170 Summer St., Boston, Mass.  
 Fraunfelder, Lewis D., 875 Main St., Buffalo, N. Y.  
 Fry, Harry Shipley, 2539 Stanton Ave., Cincinnati, O.  
 Gilbert, Frederick Chester, Eilers Plant, Pueblo, Colo.  
 Haff, Max M., Box 340 Niagara Falls, N. Y.  
 Hance, Harry T., 1093 E. Long St., Columbus, Ohio.  
 Harriman, Caleb S., North Wilmington, Mass.  
 Hartmann, Ferdinand J., 906-910 Sycamore St., Cincinnati, O.  
 Hodgen, Jos. Duprey, 1005 Sutter St., San Francisco, Cal.  
 Holm, M. L., Northwestern Univ. Bldg., 39 Dearborn St.,  
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 Ittner, Martin Hill, care Colgate & Co., Jersey City, N. J.  
 Jones, Harry C., Johns Hopkins Univ., Baltimore, Md.  
 Kofoid, R. N., 44 Lewis Block, Buffalo, N. Y.  
 Lachman, Charles, 1732 Pacific Ave., San Francisco, Cal.  
 Lawrence, John Whitaker, 3943 Indiana Ave., Chicago, Ill.  
 Locke, James, Massachusetts Institute of Technology, Boston,  
 Mass.  
 Mannhardt, Hans, 1406, 103 State St., Chicago, Ill.  
 Martin, L. W., Lynchburg, Va.  
 Mihalovitch, Sidney F., 514 Pearl St., Cincinnati, O.  
 Ober, Julius E., 748 Tremont St., Boston, Mass.  
 Pfiffer, Albert George, 155 E. 75th St., New York, N. Y.  
 Pickard, Glenn H., 400 Manhattan Ave., New York.  
 Porter, Albert B., 1232 Forest Ave., Evanston, Ill.  
 Price, Robert Coleman, Blacksburg, Va.  
 Riley, William Calvin, 33 Flood Building, San Francisco, Cal.  
 Robertson, J. H., 535 Garfield Bldg., Chicago, Ill.  
 Rockwell, George Ward, Sault Ste. Marie, Ont.  
 Schmitt, Walter, 584 W. Chicago Ave., Chicago, Ill.  
 Sullivan, Arthur L., Durham, N. H.  
 Van Wilson, Raymond, 2400 Ridge Road, Berkeley, Cal.

Wilding, Wilbur S., New York University, University Heights,  
New York, N. Y.

Zabriskie, Christopher B., 100 William St., New York, N. Y.

CHANGES OF ADDRESS.

Abbott, F. L., Box 71, Mt. Vernon, O.

Arsem, Wm., 8 Martin St., Schenectady, N. Y.

Bennett, Frank W., 26 Broad St., Boston, Mass.

Goodmar, Julian H., Yorkshire College, Leeds, England.

Gruener, Hippolyte, 43 Knox St., Cleveland, O.

Guiterman, E. W., Supt. Passaic Print Works, Passaic, N. J.

Kiessig, C. H., 96 Maiden Lane, N. Y. City.

Marshall, John, Dept. of Medicine, Univ. of Pennsylvania,  
Philadelphia, Pa.

Melcher, Arthur C., 58 Bowen St., Newton Centre, Mass.

Neher, F., care Library of Princeton University, Princeton, N. J.

Pierson, W. C., 210 Woodward Ave., Atlanta, Ga.

Rudnick, Paul, 4956 Vincennes Ave., Hyde Park, Chicago, Ill.

Runyan, E. G., Hutchin's Bldg., 10th and D. Sts., N. W., Wash-  
ington, D. C.

Rust, Robert R., care of Prime Western Spelter Co., Gas, Kans.

Saxe, S., 107 Manhattan Ave., N. Y. City.

Sharples, Philip P., 26 Broad St., Boston, Mass.

Sharples, Stephen P., 26 Broad St., Boston, Mass.

Thompson, Firman, State College, Pa.

Tolman, L. M., 1900 3rd St., N. W., Washington, D. C.

Turner, H. J., Oak Lane, Philadelphia, Pa.

Vorce, Lafayette D., Waller St., Dakota, Ill.

Wakeman, Alfred J., Green's Farms, Conn.

ADDRESS WANTED.

Batchelder, G. N., formerly of Box 241, Oxnard, Cal.

DECEASED MEMBER.

Charles Martin Stillwell died January 11, 1903, at his home in Brooklyn. He has been for twenty-five years a member of the firm of Stillwell & Gladding, the oldest firm of analytical chemists in New York City.



## MEETINGS OF THE SECTIONS.

## CINCINNATI SECTION.

Since last reported the meetings of the Cincinnati Section have been as follows:

Ninety-fourth meeting, October 8th: "An Examination of Podophyllin," by H. M. Gordin and C. G. Merrell; read by Rolland H. French. "Ana- and Meta-bromtetrahydroquinoline," by G. A. Gray. "A Chemical Method for Determining the Quality of Limestones," by Alfred M. Peter; read by Thomas Evans.

Ninety-fifth meeting, November 12th: "The Action of Methyl Magnesium Iodide upon Azoxybenzene," by Thomas Evans.

Ninety-sixth meeting, December 10th (annual meeting): "On the Need of a More Careful Chemical Supervision of Municipal Supplies," by L. L. Watters, of New York; read by the secretary.

At the annual meeting the following officers for 1903 were elected: *President*, H. E. Newman; *Vice-Presidents*, J. Everhard Weber and Sigmund Waldbott; *Secretary*, J. F. Snell; *Treasurer*, B. M. Pilhashy; *Executive Committee*, F. J. Baringer, J. W. Ellms and T. D. Wetterstroem; *Representative in the Council*, Thomas Evans.

With a view to increasing the general interest of the meetings of the Section it has been decided to have presented at each meeting of the present year a review of the most important advances in chemistry described in the literature of the preceding month.

J. F. SNELL, *Secretary*.

## NORTHEASTERN SECTION.

The fortieth regular meeting of the Northeastern Section was held at the "Tech. Union", Boston, at 8.00 P.M., December 19, 1902, President A. H. Gill in the chair. About 150 members were present. Dr. Carl Otto Weber, of Manchester, England, gave a very interesting talk on "India Rubber, Its Chemical and Technical Problems", in which he discussed the preparation of crude rubber from the milk as it comes from the trees; the composition of crude rubber; the chemical constitution of polyprrene,  $(C_{10}H_{16})_n$ , the chief constituent of rubber; possible methods for the synthetical preparation of rubber; vulcanization, etc., showing how theoretical considerations can be applied to the solution of the many technical problems which arise in the manufacture of rubber goods.

ARTHUR M. COMRY, *Secretary*.

## PHILADELPHIA SECTION.

At the meeting of the Philadelphia Section of the American Chemical Society on October 16th, John Marshall was elected presiding officer to fill the vacancy caused by the resignation of Henry Leffmann. George Auchy presented a paper on "The Rapid Determination of Molybdenum in Steel."

At the meeting of the Section, on November 20th, John Marshall and H. W. Jayne were elected councilors for the ensuing year.

P. A. Maignen presented a paper on "The Purification of Water."

At the meeting of the Section on December 18th D. K. Tuttle presented a paper on "The Methods for Refining the Precious Metals in Use at the Mint."

J. Merritt Matthews outlined "The Taylor Process for the Manufacture of Butter by Absorbing the Watery Portions of the Cream."

F. R. DODGE, *Secretary*.

## CHICAGO SECTION.

The December meeting of the Section was held in the rooms of the Chicago Drug Trade Club, on the evening of December 10th, at which time a very interesting informal talk was given by William Hoskins on the "Electrolytic Manufacture of Carbon Bisulphide."

The January meeting (annual) was held at the above-named place on the evening of the 14th inst. Dr. J. H. Long, president of the Society at large, gave a very entertaining and interesting synopsis of the transactions of the twenty-seventh annual meeting of the Society held at Washington, D. C. The following officers were also elected for the ensuing year: *Chairman*, W. A. Puckner; *Vice-President*, Prof. Alex Smith; *Secretary*, W. A. Converse; *Treasurer*, C. W. Patterson; *Member of Executive Committee*, S. T. Mather; *Councillors*, Edw. Gudeman and W. A. Converse.

W. A. CONVERSE, *Secretary*.

## WASHINGTON SECTION.

At a recent meeting the following officers were elected: *President*, Frank K. Cameron; *First Vice-President*, E. E. Ewell; *Second Vice-President*, S. S. Voorhees; *Treasurer*, F. P. Dewey; *Secretary*, J. S. Burd. These officers with the following constitute the *Executive Committee*: W. D. Bigelow, L. S. Munson, L. M. Tolman, W. F. Hillebrand, and H. N. Stokes.

L. S. MUNSON, *Secretary*.

## Proceedings.

### **FIFTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.**

I have received the following communication, dated December 3, 1902, from Dr. George Pulvermacher, Secretary of the Fifth International Congress of Applied Chemistry to be held in Berlin, beginning May 31, 1903, with the request that it be published in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY:

"The preparations for the Fifth International Congress of Applied Chemistry, which will meet in Berlin during Whitsuntide of this year and which will be the first of its kind on German soil, are advancing in a satisfactory manner. All expectations with reference to a successful session will no doubt be fulfilled to the greatest degree. The membership of the general committee and the organization committee has increased to about 150. We find as members of the general committee the Imperial Chancellor, all the secretaries of the various States and individual members of the same, the presidents of the Imperial Health Department, of the Patent Office as well as the Imperial Insurance Department, the ministers of the German Confederate States, almost all Prussian provincial ministers, representatives of many Prussian authorities and representatives of all German Confederate States. Furthermore, twelve members of the high courts, six members of the municipal council and common council, with the Chief Burgo-master and presiding officer of the common council at the head, and numerous representatives of various industries.

"About 60 of the most prominent representatives of German science and industry compose the Organization Committee and are making the requisite arrangements. An extensive fund for

the expenses of the Congress has been subscribed and is in the hands of the treasurer of the Congress, Deputy Doctor Böttinger.

"The foreign States whose Governments received notice of the Congress through diplomatic channels and who were requested to which are in constant communication with the Organization Committee in Berlin. A large attendance both from European and foreign countries is expected.

"The work of the Congress will be done in 11 sections. The President of the Congress, Prof. Dr. Otto N. Witt, in conjunction with the presiding officers of the individual sections, has fixed the basic principles for the scientific arrangement of the Congress. The sections have been divided as follows:

"(1) Analytical Chemistry, Apparatus and Instruments. Presiding officer, Prof. Dr. G. von Knorre, Charlottenburg, Technische Hochschule.

"(2) Chemical Industries of Inorganic Products. Presiding officer, Dr. Heinecke, Berlin, N. W., Wegelystr.

"(3) Metallurgy and Explosives. Presiding officer, Prof. Dr. J. Weeren, Charlottenburg, Stuttgarterplatz, 13.

"(4) Chemical Industries of Organic Products: (a) Organic Preparations Including Tar Products. Presiding officer, Prof. Dr. H. Wichelhaus, Berlin, N. W., 40, Grosse Querallee, 1; (b) Dyes and Their Application. Presiding officer, Dr. Lehne, Grunewald, Trabnerstr., 9.

"(5) Sugar Industry. Presiding officer, Prof. Dr. Herzfeld, Grunewald, Gillstr., 12.

"(6) Fermentation Industries and Starch Manufacture. Presiding officer, Prof. Dr. H. Delbruck, Berlin, W., 15, Fasanenstr., 44.

"(7) Agricultural Chemistry. Presiding officer, Prof. Dr. Wagner, Darmstadt.

"(8) Hygiene, Medical and Pharmaceutical Chemistry, Foods. Presiding officer, Dr. E. A. Merck, Darmstadt.

"(9) Photochemistry. Presiding officer, Prof. Dr. A. Miethe, Charlottenburg, Kantstr., 42.

"(10) Electrochemistry and Physical Chemistry. Presiding officer, Dr. H. T. Böttinger, Elberfeld.

"(11) Judicial and Economic Questions Associated with Chem-

ical Industries. Presiding officer, Dr. C. A. Martius, Berlin, W., 9, Vossstr., 12.

"These sections have been formed and have held sessions in which all matters placed before them have been discussed. Each section will submit certain questions of general and international importance for which referees and co-referees have been appointed and whose treatment will include a discussion as well as an eventual resolution which will be placed before the Congress in its final general session. Furthermore, each section has already received a number of papers from scientists both local and foreign. The three general sessions will include the official opening and closing addresses, and a number of detailed lectures by prominent representatives of the sciences and industries of different countries.

"A series of especially important questions in the field of analytical chemistry is now under consideration by a special international commission.

"A separate exhibit of apparatus and preparations will not be held by the Congress. It is, however, certain that the members will have numerous opportunities to become acquainted with improvements in the various provinces of chemistry. Lectures with demonstrations will be allowed in the sessions of the individual sections. Both the general section sessions will be held in the hall of the Reichstag. Only Section 10, Electrochemistry, and Physical Chemistry, will, on account of the experiments connected with the addresses, hold its sessions in the auditorium of the Physical Institute.

"A local committee has been formed, of which Dr. J. F. Holtz is chairman. An extensive program of entertainments has been prepared. An informal meeting at some suitable place has been planned for the evening of June 2nd, after the meeting in the hall of the Reichstag. A banquet and a commers will be held during the week. The city of Berlin will give a festival in honor of the members of the Congress. A performance at the opera house and a garden festival are also planned. An excursion to various points of interest in the vicinity of Berlin will close the week.

"Invitations to the Congress, which contain all details of interest to those who will participate, will be sent during January to the addresses collected during the last two years, from all countries of the world. About 50,000 copies will be distributed.

"Communications and inquiries concerning the Congress should be addressed to the bureau, Charlottenburg, Marchstrasse, 21."

Since the publication of the first list of the American Committee, the following changes have been made: M. E. Jaffa, of the University of California, present address Middletown, Conn., has been appointed chairman of Section 8, in place of Dr. W. O. Atwater, and Dr. Leo Baekeland, Snug Rock, Yonkers, N. Y., chairman of Section 9, in place of Dr. L. H. Friedburg.

Word has been received from Dr. Pulvermacher, Secretary of the Congress, that circulars of information, etc., have been sent to the Chairman of the American Committee for distribution to interested American chemists. Already a list of considerable magnitude of the names of such chemists has been compiled, but it is far from complete. All interested in receiving these circulars of information should address a request to that effect to the Chairman of the American Committee on Organization.

Intending members are requested to send a check for \$4.85 to Dr. H. W. Wiley, who will give a receipt therefor and transmit the amount to Berlin.

Titles of papers should be sent to the American chairmen of the various sectional committees (see this Journal, 24, 91, Proc.).

It is hoped that the interest which has already been manifested by American chemists in this congress will continue, and that next to Germany we may have the largest number of members enrolled.

H. W. WILEY.

### COUNCIL.

The Council has approved the establishment of a local section to embrace the territory covered by a seventy-mile radius from Pittsburg, Pa., and Blair Co., with headquarters at Pittsburg, to be known as the Pittsburg Section. There are now 57 members within the territory specified.

NEW MEMBERS ELECTED BETWEEN JANUARY 24, AND FEBRUARY 26, 1903.

Bedford, F. A., State Food and Dairy Dept., St. Paul, Minn.  
Bement, Alburto, 218 LaSalle St., Chicago, Ill.

Bourne, Lyman M., 120 Huntington Ave., Boston, Mass.

Bushong, F. W., 2408 Spencer Ave., Kansas City, Kans.

Canne, J. C. D., care American Beet Sugar Co., Oxnard, Cal.

Cooper, Addison, Jr., Vanderbilt University, Nashville, Tenn.  
 Costa, Henry Charles, 305 Lombard St., San Francisco, Cal.  
 Craver, Harrison Warwick, Carnegie Library, Pittsburg, Pa.  
 Cushing, Robt. P., care Kistler, Lesh & Co., Lock Haven, Pa.  
 Dreesbach, Philip, 294 S. Water St., Chicago, Ill.  
 Eckdahl, W. P., 9035 Superior Ave., S. Chicago, Ill.  
 Erhart, Wm. H., 81 Maiden Lane, New York City.  
 Ericson, Eric John, 9110 Ontario Ave., Chicago, Ill.  
 Failyer, Geo. H., Bureau of Soils, Dept. of Agr., Washington,

## D. C.

Franklin, Frederick Hovey, 212 Weybosset St., Providence, R. I.  
 Frees, Herman, 294 S. Water St., Chicago, Ill.  
 Gage, Robert B., 325 Water St., Pittsburg, Pa.  
 Gladding, Thomas S., 55 Fulton St., New York City.  
 Grout, Frank, Univ. of Minn., Minneapolis, Minn.  
 Gulbrandsen, Sverre, 325 Monmouth St., Gloucester, N. J.  
 Gutsche, Edward, Univ. of Minn., Minneapolis, Minn.  
 Hancock, Thomas J., 2458 N. Springfield Ave., Chicago, Ill.  
 Hodges, Robert S., University, Ala.  
 Hopkins, Joseph, Univ. of Minn., Minneapolis, Minn.  
 Housum, Wm. H., Supt. Tropenas Dept., Am. Brake Shoe and  
 Foundry Co., Chicago Heights, Ill.  
 Keiter, J. Warner, 3131 Garfield Ave., Kansas City, Mo.  
 Lando, Max, Univ. of Minn., Minneapolis, Minn.  
 Leich, Herbert, care Charles Leich & Co., Evansville, Ind.  
 Levi, Sol. L., 1014 N. Seventh St., Terre Haute, Ind.  
 Lundahl, Sam. A., 252 91st St., Chicago, Ill.  
 Madison, Herbert F., 806 Mahoning Ave., Youngstown, O.  
 McCormack, Harry, 820 W. Calhoun St., Springfield, Mo.  
 McGovney, Charles Samuel, West Lafayette, Ind.  
 Nef, J. Uric, Univ. of Chicago, Chicago, Ill.  
 Newfield, Joseph, Pinole, Cal.  
 Nilson, A., 294 S. Water St., Chicago, Ill.  
 North, H. B., 501 N. Henry St., Madison, Wis.  
 Norton, John H., 1304 W St., Washington, D. C.  
 Rasch, Christian A., 7859 Bond Ave., Chicago, Ill.  
 Rheinstrom, Jacob, 910 Sycamore St., Cincinnati, Ohio.  
 Robertson, Andrew, 2914 E. Main St., Richmond, Va.  
 Rose, Arthur R., Univ. of Minn., Minneapolis, Minn.  
 Russell, Bert, Univ. of Minn., Minneapolis, Minn.

Schmitt, F. W., Bozeman, Mont.  
 Schoen, Jos. E., 711 E. 50th St., 2nd Flat, Chicago, Ill.  
 Setz, Carl Frederick, 19 Block Y, Pueblo, Colo.  
 Skinner, J. Jas., Goshen Bridge, Va.  
 Slye, Ralph, Univ. of Minn., Minneapolis, Minn.  
 Smith, Lillie C., 911 Boylston St., Suite 4, Boston, Mass.  
 Steinbacher, Karl, 148 S. Seventh St., Ironton, O.  
 Thevenot, G., 294 S. Water St., Chicago, Ill.  
 Warville, Francis G., 618 W. Monroe St., Chicago, Ill.  
 Webb, Edward Nathan, 144 W. Ninth Ave., Columbus, O.  
 Weber, F. C., 114 E St., N. E., Washington, D. C.  
 White, J. A., 7650 Bond Ave., Chicago, Ill.  
 Wilkinson, Jas. F., 344 Whitehall St., Atlanta, Ga.  
 Wölfel, Herbert Elmer, 1321 Locust St., Allegheny, Pa.

#### CHANGES OF ADDRESS.

Allen, Charles R., 988 Mass. Ave., Cambridge, Mass.  
 Bahlmann, Clarence, 3201 Woodburn Ave., Cincinnati, Ohio.  
 Batchelder, Gilbert N.; Chemist Kohala Sugar Co., Kohala,  
 Hawaiian Islands.  
 Cox, Alvin J., Chemisches Institute, Breslau, Germany.  
 Davis, Charles B., 220 W. 134th St., New York City.  
 Dunn, W. A., Hollywood Hotel, Hollywood, Cal.  
 Evans, Ernest, National Steel Co., Zanesville, Ohio.  
 Ferris, Wm. S., Bureau of Soils, Dept. of Agr., Washington,  
 D. C.  
 Fitz-Randolph, R. B., Director of State Lab. of Hygiene,  
 Trenton, N. J.  
 Frank, J. W., 29 Broadway, New York City.  
 Fudge, Thomas, 397 Ave. E., Bayonne, N. J.  
 Gordon, Frederick T., U. S. Naval Dispensary, 2031 F St.,  
 N. W., Washington, D. C.  
 Guiterman, E. W., Supt. Passaic Print Works, Passaic, N. J.  
 Haynes, D. O., 8 Spruce St., New York City.  
 Hodgkins, D. Harwood, 78 South St., Newark, N. J.  
 Jones, L. J. W., care Tacoma Smelting Co., Tacoma, Wash.  
 Kebler, Lyman, F., Bureau of Chemistry, Washington, D. C.  
 Kedzie, Frank S., Agricultural College, Mich.  
 Lagai, Dr. G., Welling St., Richmond Hill, N. Y.



Levine, Edmund J., 7 Waverly Place, New York City.  
Lindmueller, Chas., 68 S. Ohio Ave., Columbus, Ohio.  
Lyon, D. A., Stanford University, Cal.  
Mills, Jos. S., 120 W. 46th St., New York City.  
Pritchard, Fred. P., 6441 Jackson Ave., Jackson Park, Chicago,

**Ill.**

Schoonmaker, H., 734 W. Ninth St., Cincinnati, O.  
Schüpphaus, Robert C., 1 Maiden Lane, New York City.  
Schweitzer, Dr. Hugo, 427 W. 117th St., New York City.  
Seidensticker, Lewis J., 178 Thornton St., Roxbury, Boston,

**Mass.**

Thayer, Harry S., Golden, Colo.  
White, J. A., 737 Warren Ave., Chicago.

**ADDRESSES WANTED.**

Collins, Ward O., formerly of 1411 Chicago Ave., Chicago, Ill.  
Drake, C. F., formerly of 4822 Lake Ave., Chicago, Ill.  
Felt, W. W., formerly of 7431 Longwood Ave., Chicago, Ill.  
O'Connell, C. J., formerly of 222 N. 2nd St., Cincinnati, Ohio.  
Primrose, H. W., formerly of Sheffield, Ala.

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**MEETINGS OF THE SECTIONS.**

**NEW YORK SECTION.**

The fifth regular meeting of the New York Section was held February 6th, at 8.15 P.M., in the Assembly Hall of the Chemists' Club, 108 West 55th St.

The following papers were presented: "A New Interrupter for Conductivity Determinations," by L. Kanolt; "The Micro-structure of Metals and Alloys," by William Campbell; "Review of Fischer's Recent Work on the Amino-acids," by V. J. Chambers.

FRANCIS D. DODGE, *Secretary*.

**NORTH EASTERN SECTION.**

The forty-first regular meeting of the North Eastern Section was held at the Lowell Building, Mass. Inst. of Technology, Boston, Friday, January 23rd, at 8 P.M., President A. H. Gill in the chair. Forty-six members were present. Mr. John Alden was elected

councilor from this Section to the American Chemical Society. The report of the Auditing Committee was presented by Dr. Henry Fay, and accepted.

Mr. Clifford Richardson, of New York, addressed the Section on "The Constitution of Portland Cement as Revealed by its Consideration as a Solid Solution," in which he first reviewed the literature of the subject, and showed that most of the ideas on the subject held at the present time were based upon theoretical considerations, unsupported by chemical or mineralogical study of synthetic preparations of the compounds of which the cement clinker is supposed to be formed. The speaker then described his own work on the preparation of a large number of synthetic compounds, and the determination of their optical properties, and comparison of these with the constituents of Portland cement. As a result of this work, the general conclusion was drawn that the industrial clinker of Portland cement consists of a solid solution, resembling an alloy, of dicalcic aluminate,  $\text{Al}_2\text{O}_3 \cdot 2\text{CaO}$ , in tricalcic silicate,  $\text{SiO}_2 \cdot 3\text{CaO}$ , as a principal constituent, with one of dicalcic and other dibasic silicates in the aluminate and ferrite as the secondary constituents. The lecture was illustrated with several lantern slides, and a large number of thin sections were shown under a petrographic microscope.

ARTHUR M. COMEY, *Secretary*.

#### COLUMBUS SECTION.

The first regular meeting of the Columbus Section was held January 14th, in the office of the Kauffman-Lattimer Wholesale Drug Co., about 20 members being present. Two papers were presented, one by Dr. C. A. Dye on "Microscopical Examination of Drugs" and one by Dr. W. E. Henderson on "Recent Work on Radio-Active Substances."

The papers at previous meetings of the season 1902-1903 have been as follows: On November 5th, "Testing Soils," by H. A. Weber, and "Experience with the Volumetric Method for Determination of Phosphoric Acid," by Ernest Bradford; on December 3rd, "Recent Developments in Metallurgical Analysis," by N. W. Lord.

C. W. FOULKE, *Secretary*.

## Proceedings.

### INTERNATIONAL COMMISSION FOR SUGAR ANALYSIS.

The name of F. G. Wiechmann, of the American Sugar Refining Co., Brooklyn, N. Y., was accidentally omitted from the list of chemists who have agreed to use the methods adopted by the commission.

### COUNCIL.

#### NEW MEMBERS ELECTED BETWEEN FEB. 26TH AND MARCH 26TH.

Affelder, O. I., 1230 Sheffield St., Allegheny, Pa.  
Alexander, D. Basil W., Post Office Box 1341, Denver, Colo.  
Bailey, H. S., Argentine, Kans.  
Bender, Lowry D. W., Versailles, Pa.  
Chamberlain, G. D., 5532 Avondale Place, Pittsburg, Pa.  
Corin, Magnus F., 334 La Salle Ave., Chicago, Ill.  
Cox, Harry J., 59 Washington St., Winchester, Mass.  
Cox, Harold N., 683 Madison St., Brooklyn, N. Y.  
Craver, Howard Hunter, 325 Water St., Pittsburg, Pa.  
Davis, Charles N., 5523 Center Ave., Pittsburg, Pa.  
Fargo, L., 1454 Fulton St., Chicago Ill.  
Fisher, Chester G., 4915 Forbes St., Pittsburg, Pa.  
Foster, J. Preston, Jennings, La.  
Freund, Robert H., 801 Sutter St., San Francisco, Cal.  
Gallup, Harry Wallace, 24 Wendell St., Cambridge, Mass.  
Gerkenmeyer, H. H., 109 S. Eastern Ave., Joliet, Ill.  
Gustafson, Carl F., Lawrence, Kans.  
Hanchett, Arthur K., Big Rapids, Mich.  
Hereth, Frank S., V. P. Searle & Hereth Co., 73 Wells St., Chicago, Ill.  
Hite, Bert Holmes, Morgantown, W. Va.

- Holmes, Fletcher B., 1108 Belmont St., Wilkinsburg, Pa.  
 Johnson, Alfred E., 9384 6th Ave., Chicago, Ill.  
 Jumper, Charles H., 1128 14th Ave., Altoona, Pa.  
 Kent, James M., M. T. High School, Kansas City, Mo.  
 Kingsbury, Newell C., Duquesne, Pa.  
 Kraft, J. E., 101 Seminary Ave., Chicago, Ill.  
 Kraus, Charles August, 1633 Arch St., Berkeley, Cal.  
 Lewis, Gilbert Newton, 7 Fairfax Hall, Cambridge, Mass.  
 Mali, Pierre, 8 Fifth Ave., New York, N. Y.  
 Maris, James B., Vendome Hotel, 62nd St. and Monroe Ave.,  
 Chicago, Ill.  
 McCabe, Charles R., 2701 Perrysville Ave., Allegheny, Pa.  
 McGee, Willford J., 227 N. Elmwood Ave., Oak Park, Ill.  
 Mills, W. Magoon, 5613 Kimbark Ave., Chicago, Ill.  
 Moore, Milton J., 208 Tarnsey Ave., Joliet, Ill.  
 Moore, Stanley H., M. T. High School, Kansas City, Mo.  
 Parsons, Arthur C., 6040 Ellis Ave., Chicago, Ill.  
 Peet, William, Peet Bros. Soap Co., Kansas City, Kans.  
 Peyser, Horace Frederick, 68 W. 47th St., New York, N. Y.  
 Powers, Irwin La Verne, 106 Pettee St., Providence, R. I.  
 Rosendale, Otto M., 515 Oregonian Bldg., Portland, Ore.  
 Russe, Frederick William, 54 Mt. Auburn St., Cambridge,  
 Mass.  
 Scammon, H. Leon, Danforth, Me.  
 Seaton, F. H., North Freedom, Wis.  
 Shields, Samuel M., Duquesne, Pa.  
 Stafford, Orin F., Eugene, Ore.  
 Strunz, F. B., 672 Summit Ave., St. Paul, Minn.  
 Taylor, Francis Owen, 338 Congress St., E., Detroit, Mich.  
 Thomas, Harry C., Braddock, Pa.  
 Thompson, Eugene T., Braddock, Pa.  
 Val Patten, E. B., 214 N. State St., Chicago, Ill.  
 Von Ende, Carl L., Post Office Box 1831, Iowa City, Iowa.  
 Walters, George D., Clairton, Pa.  
 Wilson, Fred J., 4717 Atlantic Ave., Pittsburg, Pa.  
 Wysor, Henry, Duquesne, Pa.  
 Yates, H. N., 208 Bryant St., N. Towanda, N. Y.

#### CHANGES OF ADDRESS.

- Closson, C. D., 41 State St., care Winthrop Drug & Chem.  
 Co., Chicago, Ill.

Dalton, N. N., Care Peet Bros. Mfg. Co., Kansas City, Kans.  
Doveton, Godfrey, 319 Majestic Bldg., Denver, Colo.  
Farnau, Earl F., 26 Grand Ave., Central Covington, Covington, Ky.  
Ferrero, Felice, 1441 Clay St., San Francisco, Cal.  
Junga, Adelbert, 649 11th St., Brooklyn, N. Y.  
Kern, Edward F., Care A. G. Betts, Lansingburgh, N. Y.  
Lando, Max, 936 Beech St., St. Paul, Minn.  
Levi, Sol. L., 532 Prospect Place, Avondale, Cincinnati, O.  
Marsh, Harry B., New Britain High School, New Britain, Conn.  
McCullough, J. E., 800 Howard Ave., Altoona, Pa.  
Meader, A. Lloyd, 121 S. Main St., Henderson, Ky.  
O'Neill, James O., 620 Walnut Ave., Niagara Falls, N. Y.  
Robertson, J. H., 535 Garfield Boulevard, Chicago, Ill.  
Schlisinger, Barthold E., 92 Mt. Vernon St., Boston, Mass.  
Schüpphaus, R. C., 174 Broadway, New York, N. Y.  
Zoul, Charles V., Winton Place, Hamilton Co., Ohio.  
Worden, Edward C., Chemist Clark Thread Co., Newark, N. J.

ADDRESSES WANTED.

Carman, John S., formerly of Lihne, Kanai, H. I.  
Cockrill, Irwin, formerly of Elkhorn, Mont.  
Dustin, Guy K., formerly of 3604 Lake Ave., Chicago, Ill.  
Emmens, Stephen H., formerly of 1 Broadway, New York, N. Y.  
Hart, Edwin B., care Frau Rothschild, No. 11 Steinweg, Marburg, Germany.  
Hartman, Wm. E., formerly of Kalamazoo Gas Works, Kalamazoo, Mich.  
Heckel, Frederick J., formerly of Box 1201, Butte, Mont.  
Hopkins, Matthew S., formerly of Royston Flats, North and Maryland Ave., Baltimore, Md.  
James, George W., formerly care Richards & Co., Chicago, Ill.  
Lysle, Walter S., formerly of 507 W. 112th St., New York, N. Y.  
Primrose, H. W., formerly care Tenn. C. I. & R. Co., Sheffield, Ala.  
Sims, Clough W., formerly of 1706 Polk Ave., Houston, Texas.  
Terry, John P., formerly of Box 51, Anaconda, Mont.

## MEETINGS OF THE SECTIONS.

## CHICAGO SECTION.

The March meeting of the Chicago Section was held at the rooms of the Chicago Drug Trade Club, 180 E. Randolph St., Wednesday evening the 11th, at which time a most excellent illustrated paper was read by Professor H. W. Hillyer, of the University of Wisconsin; subject "An Interpretation of the Peculiar Properties of Soap Solutions and a Suggestion for a Practical Soap Test."

There was also action taken at this meeting, making the Chicago Section self-supporting for the ensuing year, thereby not depending upon the funds of the Society at large. This was brought about by receipt of voluntary contributions from the members of the Section in sufficient amounts to cover legitimate expenses.

## CORNELL SECTION.

The first regular meeting of the newly organized Cornell Section was held in Morse Hall, Cornell University, at 8.00 P.M., on December 15th. The following papers were read and discussed: "The Alloys of Lead, Tin, and Bismuth," by Mr. E. S. Shepherd; "The Determination of the Hydrocarbons in Illuminating Gas," by Mr. J. G. O'Neill; and "Reductions with Soluble Anodes," by Mr. G. H. Burrows.

The officers elected for the year are: *President*, Professor L. M. Dennis; *Vice-President*, Professor W. D. Bancroft; *Secretary-Treasurer*, Mr. W. C. Geer; *Executive Committee*, Messrs. Dennis, Bancroft, and Geer; *Ex-officiis*, W. R. Orndorff, J. E. Teeple, and J. G. O'Neill.

The second regular meeting occurred on January 12th. Professor W. D. Bancroft addressed the Section on "The Theory of Indicators," the address being illustrated by a series of experiments which were explained by the theory of electrolytic dissociation.

The third meeting was held on the evening of February 9th. The following papers were read: "Some Properties of Hydro-nitric Acid," by Mr. A. W. Browne; "Acetic Anhydride and Water," by Mr. V. H. Gottschalk, which was presented by Professor W. D. Bancroft; and "Some Rare Earth Picrates," by W. C. Geer.

At the business session of the Section, Mr. J. W. Schade was elected member of the Executive Committee to succeed Mr. J. G. O'Neill who has left the Section.

W. C. GEER, *Secretary*.

#### PITTSBURG SECTION.

The new Section met for organization on March 3rd. The following officers were elected: *Chairman*, A. G. McKenna; *Vice-Chairman*, J. M. Camp; *Councillor*, F. C. Phillips; *Treasurer*, H. C. Beggs; *Secretary*, G. P. Maury.

G. P. MAURY, *Secretary*.

#### COLUMBUS SECTION.

A meeting of the Columbus Section was held on the evening of March 4th. The following papers were presented: "Manufacture of Artificial Sandstone," by S. V. Peppel, and a "Review of Recent Work on Silicic Acid," by E. N. Webb. Mr. Peppel's paper was of special interest, since he is conducting an extended investigation of the sand brick problem for the Ohio Geological Survey.

#### NEW YORK SECTION.

The fifth regular meeting of the Section was held Friday, March 6th, in the Assembly Hall of the Chemists' Club, 108 West 55th Street. The program for the evening was as follows: "Paints" (illustrated), by Houston Lowe: I, "The Permanent Protection of Steel and Iron" (illustrated), II, "The Chemistry and Physical Properties of Linseed Oil" (illustrated), by Maximilian Toch.

FRANCIS D. DODGE, *Secretary*.

#### NORTHEASTERN SECTION.

The forty-second regular meeting of the Section was held Friday, February 27th, at 8 o'clock P.M., at the "Tech Union," Boston, President A. H. Gill in the chair. Seventy members were present.

Dr. S. P. Mulliken, of the Massachusetts Institute of Technology, addressed the Section on "How May an Unknown Organic Compound Best Be Identified," in which he described a scheme which he has devised for identifying organic compounds, when in the pure state. The scheme consists in dividing all organic compounds first into orders according to the elements contained, which can be easily ascertained by qualitative tests; thus order 1 comprises all compounds containing C and H, or C, H, and O; order 2,

those containing N, etc. The orders are divided into sub-orders according to color, and the sub-orders into genera according to special tests, thus the genera of sub-order 1, colorless compounds of order 1 are 1, aldehydes; 2, carbohydrates; 3, acids; 4, phenolic compounds; 5, esters; 6, acid anhydrides and lactones; 7, ketones; 8, alcohols; 9, hydrocarbons and all other compounds. Special tests are also given for the individual species of each genera so that it is claimed that any organic compound may be accurately identified in much less time than by determining the composition by combustion, etc.

ARTHUR M. COMEY, *Secretary*.

#### RHODE ISLAND SECTION.

At the regular meeting of the Section, February 19, 1903, Mr. A. H. Jameson read a paper on "The Manufacture of Steel Castings by the Tropenas Steel Process."

CHAR. M. PERRY, *Secretary*.

#### WASHINGTON SECTION.

A special meeting was held on February 5th, at which Dr. M. Gomberg read a paper on "Triphenylmethyl."

The speaker gave an historical review of the work already published and also of some work which is soon to appear in print. The subjects taken up were: (1) The preparation and constitution of triphenylmethyl peroxide. (2) The preparation of the triphenylmethyl, and also of its ether and ester derivatives, the constitution of which is explained on the assumption of tetravalent oxygen. (3) The preparation and the reactions of triphenyliodomethane. (4) The salt-like character of the triphenylhalogen methanes from the chemical, and from the physico-chemical standpoint. (5) The condensation of triphenylmethyl to hexaphenylethane by means of different reagents. (6) Experimental evidence that metals split off only halogen from triphenylchloromethane.

Apparatus, and specimens of the various preparations were exhibited.

J. B. BULD, *Secretary*.



## Proceedings.

### REPORT OF THE COMMITTEE ON ENDOWMENT AND MEDAL FUND.

*Mr. Chairman and Gentlemen of the American Chemical Society:*

It gratifies me very much to be able to hand you my final report as Chairman of the Endowment and Medal Fund and to bring here for inspection the finished medal.

The history of the fund for this medal is already known to you, and I am frank to say that never have I served on a committee which has resulted so happily as this one. I have been connected with almost every movement in some capacity concerning our allied societies for the last six years and when I was asked to take charge of the Endowment and Medal Fund I did not anticipate the work would be brought to such a successful and speedy close. It must not be construed that I am responsible for this success, and it gives me much pleasure to thank our Chairman, Mr. T. J. Parker, for his assistance. Through Mr. William H. Nichols's generosity we are not only the possessors of this handsome medal, but also of 10 shares of the preferred stock of the General Chemical Co., which net us \$60 per year and that sum will pay every year for the medal and the necessary engraving.

The design and manufacture of the medal are distinctively American. The original drawing was made by an American artist, Mr. H. B. Wechsler, who in his student days received the Munich medal. The final sketch was revised and corrected by Mr. Henry M. Toch, who was a pupil of Edgar Ward, N. A., the American artist. Both Mr. Wechsler and Mr. Toch had in view the correctness of the costume of the alchemist, and the finished design is unique.

This design represents the allegorical figure of Dr. Faust, who is the alchemist portrayed in the dramatic poem of that name, by Goethe. The plaster cast and the finished medal were made by Marcus & Co., a reputable firm of jewelers on 5th Ave. and 45th

St., N. Y., and from the original plaster model a bronze replica had to be made from which the final steel die was reduced. This bronze casting is more than 1 foot in diameter and represents an intrinsic value of \$150. The firm of jewelers offered to present this to me and I replied to them that under the circumstances I could not accept it, excepting they gave me permission to present it to whomever I chose. This they did not wish to do, and I therefore accepted the large bronze model on condition that they would permit me to loan it, and I have therefore had it suitably framed and mounted and take much pleasure in loaning it indefinitely to Mr. William H. Nichols to whom this Society is forever indebted.

My statement of the financial condition of the fund is appended hereto.

DECEMBER 5, 1902.

*Receipts.*

Wm. H. Nichols .....	\$350.00	E. Hantke .....	\$5.00
Eimer & Amend .....	50.00	A. Tuckerman .....	5.00
A. Kuttroff .....	25.00	P. Austen .....	5.00
E. H. Kohnstamm .....	25.00	C. E. Pellew .....	5.00
G. N. Williamson .....	25.00	Wm. McMurtrie .....	5.00
T. C. Stearns .....	25.00	C. M. Loub .....	5.00
J. H. Wainwright .....	25.00	W. C. Alpers .....	5.00
C. F. Chandler .....	25.00	A. P. Hallock .....	5.00
W. J. Schieffelin .....	25.00	F. D. Dodge .....	5.00
Toch Bros. ....	25.00	A. A. Brenemann .....	5.00
S. A. Goldschmidt .....	25.00	W. Dreyfus .....	3.00
V. Coblenz .....	20.00	S. H. Baer .....	3.00
J. Hasslacher .....	10.00	O. H. Krause .....	3.00
J. A. Mathews .....	10.00	J. G. Lipman .....	3.00
C. von Egloffstein .....	10.00	W. Bowman .....	2.50
A. Tuckerman .....	10.00	Mr. Townsend .....	2.00
C. McLoughlin .....	10.00	O. Nagel .....	2.00
M. T. Bogert .....	10.00	P. O. Terheun .....	1.50
S. Bookman .....	10.00	I. W. Fay .....	2.00
L. W. McCay .....	10.00	Mr. LeClaire .....	1.00
Doremus .....	10.00	H. B. Hunter .....	1.00
J. V. Booraem .....	5.00	G. A. Sticht .....	1.00
J. S. Mergentine .....	5.00	R. Breves .....	1.00
D. D. Jackson .....	5.00	R. F. Allen .....	1.00
W. E. Dreyfus .....	5.00		

*Expenses.*

Marcus & Co .....	\$350.00
Stamps .....	10.19
Stenographer .....	5.00
Addressing .....	5.00
Printing .....	15.25

*Recapitulation.*

Receipts .....	\$816.35
Expenses .....	445.44
On hand.....	370.91

The amount for expenses includes the \$350.00 paid for the first medal. The \$60.00 cost for the medal of this year will accrue to the fund.

MAXIMILIAN TOCH.

I take this occasion to express my gratitude to Professor Bogert for his unceasing efforts. To the other members of the committee, Messrs. Chandler, Schieffelin, Stearns and Williamson, I wish to extend my thanks for their personal efforts and for their personal subscriptions.

As for Mr. W. H. Nichols, the donor of the medal and the fund, I would that some one else had been selected to express our thanks for his generosity. Suffice it to say, the medal and its endowment speak for itself, for the gift is worthy of the giver. It must be a source of satisfaction to Mr. Nichols to know that every year there will be an incentive throughout all the sections, not only for the production of original scientific papers but for the reading of unique treatises of a practical kind which henceforth will probably be a distinctive feature of the meetings of the American Sections.

Within the past five years industrial men have become captains of industry, and immense fortunes have been made in this country which have been unparalleled in the annals of the world's history. A period of prosperity has helped this country to such a remarkable extent that where millionaires were formerly a rarity they are now in almost countless numbers. It is a strange fact that the industrial advance in this country can be primarily traced to the application of chemistry in the various factories. Thousands of rich men owe their success to chemical industry directly or indirectly and out of all these wonderful successes that have taken place, Mr. William H. Nichols is the first captain of industry who has the honor of placing a premium on chemical science and chemical research in America.

Respectfully submitted,

MAXIMILIAN TOCH, *Chairman.*

CONDITIONS OF AWARD FOR THE WM. H. NICHOLS'S MEDAL.

The Nichols's Medal is awarded annually, by the New York Section, to the author who presents to that Section the best paper

embodying the results of original chemical research. The paper must subsequently be accepted and published in the Journal of the Society, and must be of sufficient merit to deserve the award of the medal. Competition is not restricted to members of the New York Section, or even of the Society, nor, necessarily, to those who present papers in person.

The medal for the year, ending July 1st, 1902, was awarded to Dr. E. B. Voorhees, of New Brunswick, N. J., for his paper, "Studies in Denitrification", which was published in This Journal, 24, 785.

### COUNCIL.

The Council has approved the following motion offered by Dr. A. A. Noyes:

"That the President be requested to appoint a committee of five members, representing five different branches of chemistry and so situated as to be able to attend a meeting at some central point like New York City, whose duty it shall be to consider the advisability of organizing divisions of the Society representing the various branches of chemistry, and to report thereon to the Council prior to the Cleveland meeting."

The committee appointed consists of Drs. A. A. Noyes, Wm. McMurtrie, L. P. Kinnicutt, M. T. Bogert and E. F. Smith.

The Council has also approved the following motion offered by Dr. Wm. McMurtrie:

"That the Librarian be authorized, in his discretion, to sell copies of No. 3, Vol. VI, of the Journal of the Society."

W. A. NOYES, *Secretary*.

### MEMBERS ELECTED BETWEEN MARCH 26TH AND APRIL 20TH.

Babb, Joseph S., care Westinghouse Machine Co., East Pittsburgh, Pa.

Bowey, John, Jr., East Chicago, Ind.

Bryant, A. P., 661 Winthrop Ave., Chicago, Ill.

Culver, G. E., Stevens Point, Wis.

Engle, Robt. H., 31st and Walnut Sts., Philadelphia, Pa.

Fahrig, Ernst, Commercial Museums, Philadelphia, Pa.

Fairbanks, Clair W., 3007 15th St., Washington, D. C.

Fisher, Thos. W., 1012 Penna. Ave., Tyrone, Pa.

Fitz-Williams, C. B. Raoul, 29 Henry St., Port of Spain, Trinidad, B. W. I.

Freskow, Fritz, Crockett, Cal.

Gottschalk, V. Hugo, Missouri School of Mines, Rolla, Mo.

Govers, F. X., Owego, N. Y.

Hewitt, Thomas Edwin, 331 Atwood St., Pittsburg, Pa.

Hirsh, Joseph E., 1245 85th St., Brooklyn, N. Y.

Klooz, Otis T., 395 S. Hohman St., Hammond, Ind.

Levi, Louis E., Cor. Miss. and Perry Sts., Buffalo, N. Y.

Lieban, Carl, care Mich. Chem. Co., Bay City, Mich.

Little, Franklin Alfred, 2205 Webster St., San Francisco, Cal.

McTaggart, J. R., Public Safety Bldg., Pittsburg, Pa.

Morgan, W. C., 202 Harrison Ave., Leadville, Colo.

Nielson, N. L., West Berkeley, Cal.

Orth, Henry, Jr., 1011 L St., N. W., Washington, D. C.

Page, Alexander G., Mt. Tamalpais Military Acad., San Rafael, Cal.

Quinan, Clarence, 751 Sutter St., San Francisco, Cal.

Steir, John W., care Carnegie Steel Co., Braddock, Pa.

Thompson, William, Rossland, B. C., Canada.

Van Ostrand, A. S., Braeburn, Pa.

Vavra, Joseph, Howell's, Nebr.

Walker, Claude F., Lock Box 232, Montclair, N. J.

Warren, Frederick John, 93 Federal St., Boston, Mass.

Warren, Ralph L., 93 Federal St., Boston, Mass.

Warren, Walter Burgess, 93 Federal St., Boston, Mass.

Webb, R. H., Argentine, Kans.

#### CHANGES OF ADDRESS.

Annear, J. B., Wall St., Colo.

Arnold, Fred. N., Jr., care N. K. Fairbanks Co., St. Louis, Mo.

Baltzly, Edwin Bertram, Niagara Falls, N. Y.

Blanchard, A. A., New Hampshire College, N. H.

Brown, W. B., care the Victor Chemical Works, Chicago Heights, Ill.

Catlett, Geo. F., Wilmington, N. C.

DuPont, Francis G., Montchanin, N. J.

DuPont, Irene, 788 Broad St., Newark, N. J.

Eastwood, J. P., 608 E. Williams St., Ann Arbor, Mich.

Ebaugh, W. Clarence, 76 West Second St., Salt Lake City, Utah.

- Ewell, E. E., Manager of Bureau of Chemistry, Washington, D. C.
- Fell, J. William, Asheville, N. C.
- Franklin, Arthur I., Pullman, Chicago, Ill.
- Heidenhain, H., 108 Gitschiner Strasse, Berlin, Germany.
- Hiltner, R. S., Supervising Architect's Office, Treas. Dept., Washington, D. C.
- Johnson, Geo. A., 302 Main St., Poughkeepsie, N. Y.
- Jones, F. W., 96 Downs Park Road, Clapton, London, N. E., England.
- Kiehn, Joseph F., 1848 34th Place, Brighton Park, Chicago, Ill.
- Lando, Max, 936 Beech St., St. Paul, Minn.
- Levi, Sol. L., 532 Prospect Place, Avondale, Cincinnati, O.
- Lindmueller, Charles, 968 E. Long St., Columbus, O.
- MacDowell, W. F., U. S. Public Health and Marine Hospital, Medical Division, Immigration Dept., Ellis Island, N. Y. City.
- Pickard, Glenn H., 364 W. 118th St., New York, N. Y.
- Piper, W. E., 89 Main St., Melrose, Mass.
- Plank, W. F., Room 705, V. G. I. Bldg., Broad and Arch Sts., Philadelphia, Pa.
- Pratt, J. H., 74 Broadway, N. Y. City.
- Root, Wm. W., 410 Marshfield Ave., Douglass Park, Chicago, Ill.
- Runyan, E. G., Inspector of Gas and Meters, 10th and D Sts., N. W., Washington, D. C.
- Sanders, Warren W., 62 Parker St., Gardner, Mass.
- Spayd, C. H., 9 N. 13th St., Harrisburg, Pa.
- Sullivan, Arthur L., Div. of Chem., Treas. Dept., Washington, D. C.
- Torrey, Joseph, Jr., 28 Beck Ave., Akron, O.
- Wrampelmeier, T. J., 2415 Bowdel St., Berkeley, Cal.
- Youtz, L. A., 672 Lawe St., Appleton, Wis.

## ADDRESSES WANTED.

- Benson, D. H., formerly Box 145, Jacksonville, Fla.
- Blount, Hunter H., formerly 6 East 32nd St., N. Y. City.
- Drake, C. F., formerly 4822 Lake Ave., Chicago, Ill.
- Duryea, Chester B., formerly 34 Gramercy Park, N. Y. City.
- O'Connell, C. J., formerly 222 W. 2nd St., Cincinnati, O.
- Prindle Harry B., formerly 90 W. Broadway, N. Y. City.

Smith, Burnett, formerly 211 Franklin, Univ. of Pa. Dormitories, Philadelphia, Pa.

Watson, Henry, E. G., formerly 5333 Wayne Ave., Germantown, Philadelphia, Pa.

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DECEASED MEMBERS.

Mr. Alonzo P. Howard, of Boston, Mass., associate in the Society since March, 1898, died August 26, 1902.

W. Herbert C. Kohl, of Craigsville, Va., member of the Society since February, 1901, died November 10, 1902.

Mr. W. C. Tiffany, of New York City, member of the Society since 1896, died November 24, 1902.

EDWARD ROBINSON SQUIBB.

After a brief illness, there passed away at his home in Brooklyn, October 25, 1900, Edward Robinson Squibb, one of the foremost representatives of the American chemical and pharmaceutical industries.

Edward Robinson Squibb was born in Wilmington, Del., on July 4, 1819. He studied pharmacy between the years 1837-1842, preparatory to the study of medicine. In 1844 he graduated from the Jefferson Medical College, Philadelphia, Pa., and almost immediately thereafter was appointed surgeon in the U. S. Army, and attached to the "Perry," on board which he served during the Mexican war that was then in progress. At the close of the war he was appointed Assistant Director of the United States Naval Laboratory at Brooklyn, where his already remarkable ability and precise knowledge were utilized in the preparation of medical supplies of a high standard of excellence.

After remaining in the government employ for a year or so, he resigned his position to become the manufacturing partner in the firm of Thomas E. Jenkins & Co., of Louisville, Ky., known as the Louisville Chemical Works. At the end of the year, however, Dr. Squibb opened for himself a laboratory in Brooklyn, for the avowed purpose of supplying pure pharmaceutical chemicals. His recognized ability and integrity secured for him in advance the patronage of the medical department of the U. S. Army for the supply of chemicals of a quality equal to those prepared at the Naval Laboratory. From the very beginning, he devoted most attention to the manufacture of ether for surgical purposes, and he was probably the first to utilize steam heat in its manufacture.

His establishment was scarcely under way, when, following a violent explosion of ether, it was burned to the ground, Dr. Squibb being severely burned. The laboratory was rebuilt at once, Dr. Squibb, even while convalescing, making the plans of the new building. Altogether, the laboratory was destroyed three times by fire. In no wise discouraged by these reverses, Dr. Squibb persevered in building up a business which stands as a monument to his ability, industry, and integrity. It needed but his label on a package to afford the most implicit assurance as to the quality of the contents—in fact the name "Squibb" stood for the highest attainable purity in medicinal chemicals. In addition to his great activity as a manufacturer, Dr. Squibb was an indefatigable investigator as well as a most prolific writer, having written scores upon scores of papers on chemical and pharmaceutical topics. All his papers bear the evidence of thorough knowledge, and have a convincing directness. The perhaps most valuable papers written by him are those on ether, alcohol, and chloroform. That on ether was published in 1856, and gave a complete description of the apparatus employed and of the use of steam in its manufacture. That on chloroform was published in 1857, and besides minutely describing his process of manufacture, it also gave a detailed description of the impurities, and of tests to which a good article should respond. In addition to these, he wrote a number of highly important papers embodying the results of a long series of investigations regarding the manufacture of absolute alcohol, and also published an elaborate alcohol table having seven divisions showing the relative specific gravities at  $15\frac{1}{2}^{\circ}$  C. ( $= 60^{\circ}$  F.) and at  $25^{\circ}$  C. ( $= 77^{\circ}$  F.); percentages by weight, volume, etc.; the weight of 1 gallon of alcohol at  $15\frac{1}{2}^{\circ}$  C. ( $= 60^{\circ}$  F.) in grams, grains, and avoirdupois; next the weight of 40 gallons in pounds to the nearest half-pound, and lastly the weight of 1 pint at  $15\frac{1}{2}^{\circ}$  C.

The following list comprises practically all the papers written on strictly chemical subjects by the gifted author:

1853—Ethereal Oil and Spirit-Ether Compound.

1856—Improved Method of Carbon and Hydrogen Determination in Organic Elementary Analysis.

Process of, and Apparatus for, the Manufacture of Ether by Steam.



- 1857—Manufacture of Ethereal Oil.  
Manufacture, Impurities, and Tests of Chloroform.
- 1858—Purification of Liquids in the State of Vapor, and New Apparatus for Rectifying Spirits, with drawings of apparatus used for alcohol on the large scale, and by which absolute alcohol may be made at a nominal expense.
- 1859—Notes on Silver Nitrate, Ferrous Iodide, Mercurous and Mercuric Iodides, Morphine Sulphate and Zinc Chloride.
- 1860—Sodium and Iron Pyrophosphate.  
Solution Iron Persulphate.  
Ethereal Oil—Regarding the changes which take place in it on keeping, and how they may be prevented.
- 1862—Experiments on the Effect of Bleaching Processes on Morphine Sulphate.  
Statistics and Assays on Virgin Scammony.
- 1864—Manufacture of Potassium Permanganate.
- 1868—Contamination of Hydrochloric Acid with Sulphuric Acid and Other Sulphur Oxides.  
Note on the So-called Carbolic Acid, or Coal-tar Creosote.
- 1871—Note on the Manufacture of Chloral Hydrate, with Special Reference to the Best Methods of Crystallizing, and Determination of the Boiling-point.  
Commercial Bicarbonate of Sodium.
- 1872—Note on the Manufacture of Citrate of Bismuth and Ammonium.
- 1873—Note on Buying Alcohol or Distilled Spirits. With alcohol tables.  
General Apparatus Stand, Upright Condenser, Pinchcock and Burette Stand.
- 1878—Preparation of Hydrobromic Acid.
- 1882—Process for Making Sodium Salicylate.  
Method of Opium Assay.  
Improved Fluckiger's Method of Opium Assay.  
Assay of Cinchona.
- 1884—Paper on Absolute Ether, Its Preparation, Specific Gravity, etc. With a table showing the specific gravity of mixtures of alcohol with ether.  
Absolute-Alcohol Test.  
Exhaustive Paper on Alcohol.  
Testing Urine for Albumin.  
Apparatus for Determining Urea in Urine,—with table showing the percentage of urea from nitrogen evolved.

1885—Assay of Cocaine.

Preparation of Citrate of Iron and Quinine, and Its Constituents.

Method of Assay of Cocaine, with a Description of a Separator for the Extraction of Alkaloids.

1887—New Process of Manufacture and Assay of Cocaine Hydrochlorate, with an Examination of Market Brands by Various Processes.

Improved (Specially Modified) Opium Assay.

Cost of Manufacture, Commercial Quality, and Character of Impurities of Cocaine Hydrochlorate.

These papers, however, constitute but a small number of those actually written, by far the greater number having been devoted to pharmaceutical topics. They fully demonstrate, however, the exceeding activity and versatility of the writer.

Besides being a member of the American Society, which he joined in 1877, Dr. Squibb was a member of several medical associations, the Metropolitan Museum of Art, the Linnaean Society of New York, the Philosophical Society of Philadelphia, a life member and Fellow of the Brooklyn Institute of Arts and Sciences, a Fellow of the American Association for the Advancement of Science, honorary member of the Pharmaceutical Society of Great Britain, life member of the American Pharmaceutical Association, and of many minor societies.

Dr. Squibb was highly esteemed by all who knew him as a man of great erudition, rare probity, and innate modesty. His indomitable perseverance, kindness, and simplicity endeared him to all who came in contact with him.

CHARLES A. DOREMUS.

ALFRED J. COHN.

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## MEETINGS OF THE SECTIONS.

### CALIFORNIA SECTION.

*Initial Meeting.*—Pursuant to a call made by Edmond O'Neill, the members of the American Chemical Society resident in California met in San Francisco on November 8, 1901, and organized themselves into a local section according to the constitution of the Society. The officers elected were Edmond O'Neill, *Chairman*; Felix Lengfeld, *Vice-Chairman*, and T. Michaelis, *Secretary-Treasurer*. The following by-laws were adopted to govern the local section.

1. The name of this Section shall be the California Section and all members of the American Chemical Society resident in the State of California shall be members of the Section.

2. The officers of the Section shall be a Chairman, Vice-Chairman and Secretary-Treasurer, and an Executive Committee to consist of the above three officers. The Executive Committee is to have general control of the affairs of the Section and to make all arrangements for meetings. The Chairman and Vice-Chairman and Secretary-Treasurer are to perform all the duties usually pertaining to their respective offices, as determined by the Executive Committee.

3. The officers elected at the meeting shall hold office until the second meeting held after the thirty-first of August, of each year or until their successors have been elected.

4. Officers shall be elected annually at the first meeting held after the thirty-first of August, the election to be by ballot in the usual way.

5. There shall be at least six meetings held each year, the time and place to be determined by the Executive Committee.

6. At each meeting the Chairman shall appoint a committee of three to arrange for a program for the second meeting in the future.

7. Papers are not to exceed thirty minutes in length.

The first meeting was held in San Francisco December 13, 1901, and the paper of the evening was by E. C. Burr on the beet-sugar industry. J. M. Stillman was elected councilor for the Section.

Six meetings were held during 1902. The following papers were presented: Feb. 21—W. S. Young, "Inhibition of Chemical Reaction by Foreign Substances." At this meeting H. E. Miller was appointed Secretary-Treasurer vice T. Michaelis resigned. March 29—Felix Lengfeld, "Hydroxylamine and Some of Its Derivatives." May 3—W. C. Blasdale, "Some Recent Applications of the Dissociation Theory." Sept. 13—Arthur Lachman, "The Color of Iodine in Solution." At this annual meeting the following officers were elected: E. C. Burr, *Chairman*; Felix Lengfeld, *Vice-Chairman*; H. E. Miller, *Secretary-Treasurer*; and J. M. Stillman, *Councilor*. The attention of the members was called to their loss by the death of G. M. Richardson, and a com-

mittee was appointed which drew up and presented appropriate resolutions. Nov. 15—Edmond O'Neill, "An Account of the Texas Petroleum Field." Dec. 20—J. M. Stillman, "Some Limiting Conditions in the Purification of Feed-Water."

A meeting was held in San Francisco, January 24, 1903, and took the form of a "Kneipe." The Section had a celebration to rejoice over its rapid growth and there was no set program but various members contributed to the entertainment of the evening, avoiding all technical or scientific subjects.

The ninth meeting was held in San Francisco, February 28, 1903, and the paper of the evening was by F. G. Cottrell, who gave an interesting description of some of the European laboratories, their masters and their methods. Thirty-nine members and guests were present at the dinner immediately preceding the meeting.

The tenth meeting was held Saturday, April 4th, in Tortoni Restaurant, 111 O'Farrell St., San Francisco. The paper of the evening was by Mr. C. A. Krause, of the University of California, on "The Properties of Solutions in Liquid Ammonia." A dinner preceded the meeting in the same place.

Seventy responses have been received to the inquiry as to occupation or special chemical work, and the following is the classification: Educational 23, Commercial 8, Consulting 6, Sugar 6, Oil and Asphaltum 5, Explosives 4, Students 4, Government and Municipal 3, Practising Physicians 2, Acid 2, Bacteriology 2, Malt-ing and Brewing 1, Railroad 1, Fertilizers 1, Foundry 1, Wine 1. The distinction made between commercial and consulting is that the former have laboratories for general work and, of these, three include assaying.

The membership of the Section now numbers ninety. Until further notice a lunch club composed of members and their friends will meet every Wednesday at Tortoni, where from 12 to 2 you are sure to find good company.

HARRY EAST MILLER, *Secretary*.

#### NORTHEASTERN SECTION.

The forty-third regular meeting of the Section was held at the "Tech Union," Massachusetts Institute of Technology, Boston, Tuesday, March 31, at 8 P.M., President A. H. Gill in the chair. About forty-five members were present. Prof. Charles F. Mabery, of Cleveland, Ohio, presented a paper, entitled "A Résumé of the Composition of Petroleum," in which, after a

historical introduction, the lecturer described the work carried on under his direction during the last ten years in the laboratories of the Case School, Cleveland, and discussed the results obtained, from which the general conclusion was drawn that petroleum can be defined as a mixture of a few series of hydrocarbons of the general formula,  $C_nH_{2n+2}$ ,  $C_nH_{2n}$ ,  $C_nH_{2n-2}$ , and  $C_nH_{2n-4}$ , and products from different fields differ only in the proportion of the series contained in them. A great field for chemical research yet remains in ascertaining the structure of the members of the series above mentioned, and also of the so-called asphaltic hydrocarbons, which cannot be distilled without decomposition.

ARTHUR M. COMEY, *Secretary*.

#### CHICAGO SECTION.

The April meeting of the Section was held on Wednesday eve, April 8th, at the rooms of the Chicago Drug Trade Club, 180 Randolph St., at which time a very interesting paper was read by Prof. L. M. Dennis, of Cornell University, on "The Determination of Benzene in Illuminating Gas."

W. A. CONVERSE, *Secretary*.

#### NEW YORK SECTION.

A special meeting of the Section was held Friday, March 27th, at 8.15 P.M., in the Assembly Hall of the Chemists' Club, 108 West 55th Street. The program for the evening was as follows: Maximilian Toch, "The Chemistry and Physical Properties of Linseed Oil."

The seventh regular meeting of the Section was held Wednesday, April 8th. The program for the evening was as follows: Charles Baskerville, "The Rare Earth Crusade: What It Portends, Scientifically and Technically;" John A. Mandel, "The Structure of the Proteid Molecule."

FRANCIS D. DODGE, *Secretary*.

#### CINCINNATI SECTION.

At the ninety-seventh meeting of the Cincinnati Section, January 14th, the following papers were presented: "A Case of Quadrivalent Oxygen," by H. S. Fry; "Recent Progress towards the Absolute Zero," by H. E. Newman.

At the ninety-eighth meeting of the Section, February 11th, Dr. Alfred Springer presented a review of the important advances in chemistry described in the literature of the preceding month. The subjects discussed were Ramsay's theory of the cause of the Aurora Borealis, Gautier's investigations on the distribution of

arsenic in animate nature, J. J. Thomson's description of the phenomena of radioactivity, Neumann and Mayer's work on iron in diabetic urine and Connstein, Hoyer and Wartenburg's observations of the fermentative hydrolysis of fats. The review was opened with a humorous introduction entitled "Methylxanthine Genitum ab Uncinariase." Dr. W. H. Crane, on Dr. Springer's suggestion, gave an outline of the chemical phenomena connected with diabetes.

The ninety-ninth meeting of the Section was held March 11th. The following papers were presented: "Unsoundness in Hydraulic Cements," by J. W. Ellms; "The Action of Magnesium Alkyl Halides upon Quinones," by Arthur Lowenstein. The Section voted to suggest that the summer meeting of the Society be held in the latter part of August instead of the latter part of June.

The one hundredth meeting of the Section was held April 8th, when a joint lecture on "Coffee in General—Ariosa in Particular" was delivered by Drs. Alfred Springer, Thomas Evans, and Wm. H. Crane. The lecture was copiously illustrated with charts, specimens and lantern projections.

J. F. SNELL, *Secretary*.

#### NEBRASKA SECTION.

A meeting was held in Room 4, of the Chemical Laboratory of the University of Nebraska, Monday, March 30, 1903, at 8 P.M. Program: "The Physiological Chemistry of Uric Acid," by Arthur Charles Stokes.

R. S. HILTNER, *Secretary*.

#### WASHINGTON SECTION.

The 142nd regular meeting was held Thursday, April 9, 1903, at 8 P.M., in the Assembly Hall of the Cosmos Club, 1520 H Street, N. W. Program: Professor Edgar F. Smith, "New Results in Electrochemical Analysis."

An adjourned meeting was held Saturday, April 18, 1903, at 8 P.M., in the Chemical Lecture Hall, Johns Hopkins University, Baltimore, Md. Program: H. N. Morse, "Recent Progress in the Making of Cells for the Measurement of Osmotic Pressure;" H. C. Jones, "The Effect of One Associated Solvent on the Association of Another Associated Solvent;" F. K. Cameron and Geo. H. Failyer, "Determination of Small Amounts of Potassium;" F. K. Cameron and J. F. Breazeale, "The Action of Certain Acids and the Corresponding Calcium and Potassium Salts upon Seedlings of Corn."

J. S. BURN, *Secretary*.

## Proceedings.

### COUNCIL.

#### NEW MEMBERS ELECTED BETWEEN APRIL 20TH AND MAY 20TH.

- Asbury, S. E., Dept. of Agr., Raleigh, N. C.  
Banks, Harry P., 1119 W. Adams St., Chicago, Ill.  
Bird, Walter C., 910 S. Spaulding Ave., Chicago, Ill.  
Blum, William, 223 W. Penn St., Germantown, Phila., Pa.  
Bowen, James Walter, Toledo, Iowa.  
Carle, J. F., Bessemer, Ala.  
Chanute, C. D., 6047 Jefferson Ave., Chicago, Ill.  
Doxrod, Christian Lund, Christiana, Norway.  
Ellis, Ralph J., 8 Clematis St., Winchester, Mass.  
Ellis, Thomas W., 5124 Holmes St., Pittsburg, Pa.  
Fouch, Thos. B., Winston, N. C.  
Grider, Noah C., Stanford University, Cal.  
Hanson, Martin, care of Royal Baking Powder Co., Brooklyn,  
N. Y.  
Hawkes, Albert W., Room 816, 135 Adams St., Chicago, Ill.  
Hazard, Elmer Clarke, Shrewsbury, N. J.  
Hazen, Charles R., Collinswood, O.  
Heath, George Millard, Big Rapids, Mich.  
Herzstein, M., 801 Sutter St., San Francisco, Cal.  
Holland, Hazel, Charlotte, N. C.  
Hooker, A. H., 9531 Winchester Ave., Chicago, Ill.  
Horn, A. C., Grand Island, Neb.  
Huddle, Wiley J., Madison, Wis.  
Jacobson, I., Station P, Cincinnati, O.  
Jurist, Benjamin, 110-112 Delancey St., New York, N. Y.  
Levy, Henry Wolff, 423 B Chancery Lane, Melbourne, Victoria.  
McCready, Ernest B., 414 Turner St., Allentown, Pa.  
Millwood, J. P., 246 Willoughby Ave., Brookline, Mass.  
Mommers, Richard, Pekin, Ill.  
Nish, Jas. C., 394 Washington St., Lynn, Mass.

Oakley, Albert E., 9 North Ave., Braddock, Pa.  
 Olshausen, B. A., Columbia University, New York, N. Y.  
 Palmer, Irving A., 310 1/2 W. 9th St., Pueblo, Colo.  
 Patterson, Edmond V., University Club, Baltimore, Md.  
 Petraeus, Carl V., Iola, Kans.  
 Rheinus, B., 33d St. and 10th Ave., Paterson, N. J.  
 Rice, William F., High School, Springfield, Mass.  
 Richter, George, 2424 S. 18th St., St. Louis, Mo.  
 Roberts, John Edward, Gayoso Hotel, Memphis, Tenn.  
 Steinmayer, Otto C., 522 Madison St., Topeka, Kans.  
 Stevenson, Reston, Chapel Hill, N. C.  
 Symmes, Whitman, 630 Harrison St., San Francisco, Cal.  
 Test, William H., 716 Brown St., Lafayette, Ind.  
 Tunnell, Raymond W., 425 W. Walnut Lane, Germantown,  
 Phila., Pa.  
 Wilhelmj, Arthur, 781 Sutter St., San Francisco, Cal.  
 Willard, Charles Turner, 43 Edward St., Worcester, Mass.  
 Wilson, Burns Alexander, 1348 Block St., Baltimore, Md.  
 Wilson, Samuel Herbert, Fairburn, Ga.  
 Wolcott, Clifford, 468 Van Buren St., Chicago, Ill.  
 Zöhe, Ludwig Alvine, Syracuse, N. Y.

#### CHANGES OF ADDRESS.

Bosart, L. W., Jr., 3423 Harvey Ave., Avondale, Cincinnati,  
 Ohio.  
 Bragg, E. B., 1745 Chicago Ave., Evanston, Ill.  
 Carpenter, Thomas B., 533 Franklin St., Buffalo, N. Y.  
 Cavanaugh, Dan J., 1400 N. 3rd St., St. Charles, Mo.  
 Clevenger, G. H., Deadwood, S. D.  
 Corse, W. M., 1283 Third Ave., Detroit, Mich.  
 Dailey, J. Glanding, care of San Carlos Copper Co., Lenares,  
 Nuevo Leon, Mex.  
 Davis, Charles B., Lion Brewery, 108th St. and Columbus Ave.,  
 New York.  
 de Benneville, James S., Yokohama, Japan.  
 Denham, Henry H., 830 Auburn Ave., Buffalo, N. Y.  
 Ebaugh, W. Clarence, 76 W. Second South St., Salt Lake  
 City, Utah.  
 Ewell, E. E., Manager German Kali Works, Atlanta, Ga.



- Fowler, Roy E., National Electrolytic Co., Niagara Falls, N. Y.  
 Fuller, Henry C., 4 Dayton St., Worcester, Mass.  
 Goldschmidt, S. A., 43 Sedgewick St., Brooklyn, N. Y.  
 Goodell, Geo. A., Mirror Lake, N. H.  
 Gray, John H., Jr., 280 Twelfth Ave., San Francisco, Cal.  
 Gross, John, Maitland, S. D.  
 Gutsche, Edw. J., Glencoe, Minn.  
 Haas, Herbert, 121 Market St., San Francisco, Cal.,  
 Haff, Max M., 138 Slater St., Ottawa, Can.  
 Harrell, George R., Kelford, N. C.  
 Hartwell, Burt L., Kingston, R. I.  
 Hero, Ann (Miss), 1213 Third St., New Orleans, La.  
 Herreshoff, J. B. F., 40 W. 69th St., N. Y. City.  
 Hewett, Foster, 5746 Howe St., Pittsburg, Pa.  
 Hibbard, P. L., 2657 North 42nd Court, Chicago, Ill.  
 Hicks, Edwin F., 1225 Park Building, Pittsburg, Pa.  
 Hughes, Louis S., 1149 Washington Boulevard, Chicago, Ill.  
 Huntington, Harwood, Appraiser's Stores, Washington St.,  
 New York, N. Y.  
 Huston, H. A., Room 134 Laclede Bldg., St. Louis, Mo.  
 Ingraham, William T., 1633 Wakeling St., Frankford, Phila., Pa.  
 Jessup, Alfred E., Tientsin, North China.  
 Johnson, Charles W., St. Joe Sta., Dekalb Co., Ind.  
 Kee, William J., Jr., care of Harrison Bros. and Co., Inc., 35th  
 St. and Gray's Ferry Road, Philadelphia, Pa.  
 Kohr, D. A., care of The Lowe Bros. Co., Dayton, O.  
 Lindmueller, Chas., 32 N. Grant Ave., Columbus, Ohio.  
 Linebarger, C. E., 2583 Hermitage Ave., Chicago, Ill.  
 Lomax, C. L., 25 Pleasant St., Everett, Mass.  
 Loudon, Archie M., Cold Spring, N. Y.  
 Lowenstein, Arthur, care of B. & O. Cement Lab., Wheeling,  
 W. Va.  
 Mahin, Edward G., 328 S. Grant St., West Lafayette, Ind.  
 Masson, Victor E., Rheims, Steuben Co., N. Y.  
 McCarthy, Maurice L., 30 Maple St., Haverhill, Mass.  
 Mersereau, Gail, care of Susquehanna Dye Works, Williams-  
 port, Pa.  
 Metcalf, W. V., Physico-Chem. Lab., University of Leipzig,  
 Leipzig, Germany.  
 Moody, Herbert R., Box 2533, Boston, Mass.

- Myers, Ralph E., 130 S. College St., Columbus, O.  
Nichols, M. F., care of Wallen Leather Co., Station A. Grand Rapids, Mich.  
Olshausen, B. A., 646 W. 15th St., Los Angeles, Cal.  
Page, A. G., 657 Bush St., San Francisco, Cal.  
Page, Robert W., 200 Chestnut St., Towanda, Pa.  
Palmer, Chas. S., 1524 Court Place, Denver, Colo.  
Parrett, B. C., Eveleth, Minn.  
Peppell, S. V., 431 W. Main St., Louisville, Ky.  
Perley, Wm. M., Bartow, Fla.  
Petsche, B. W., 60 Glenwood Ave., Yonkers, N. Y.  
Porter, Fred. B., 4911 Champlain Ave., Chicago, Ill.  
Porter, Horace C., care of National Carbon Co., Cleveland, O.  
Rockwell, G. W., Lehigh Portland Cement Co., Allentown, Pa.  
Rogers, Allen, Hampden Corner, Me.  
Root, Wm. W., 429 Hermitage Ave., Chicago, Ill.  
Ryland, Garnett, 839 W. Grace St., Richmond, Va.  
Schoen, Jos. E., 4941 Forrestville Ave., Hyde Park Station, Chicago, Ill.  
Smith, Arthur G., Winchester, Ill.  
Smith, (Miss) Lillie C., 163 Huntington Ave., Suite 3. Boston, Mass.  
Snelling, W. O., 3412 13th St., N. W., Washington, D. C.  
Starr, Henry F., 91 Mt. Pleasant Ave., Newark, N. J.  
Stewart, Andrew, 1214 K St., N. W., Washington, D. C.  
Thayer, Harry S., Telluride, Colo.  
Thompson, Firman, New Carlisle, O.  
Tibbals, W. I., 187 Canton Ave., Detroit, Mich.  
Torrey, Chas. A., Lynnfield, Mass.  
Touceda, Enrique A., Albany, N. Y.  
Touzalin, L. A., 1600 W. Monroe St., Chicago, Ill.  
Van Gelder, Arthur P., Emporium, Kans.  
Vavra, Jos., care of Longmont Sugar Co., Longmont, Colo.  
Wade, E. M., 318 E. 1st St., Los Angeles, Cal.  
Walker, Percy, 731 Jefferson Ave., Scranton, Pa.  
Wilding, W. S., 25 Cherry St., Elizabeth, N. J.  
Willard, Chas. T., 1 State St., Schenectady, N. Y.  
Zimmele, H. B., 59 N. 11th St., Newark, O.

## ADDRESSES WANTED.

Beatty, Leon O., formerly 606 W. 113th St., N. Y. City.

O'Connell, C. J., formerly 222 N. 2nd St., Cincinnati, Ohio.

## MEETINGS OF THE SECTIONS.

## NORTH CAROLINA SECTION.

The spring meeting of the Section was held in the Chemical Lecture Room of the University of North Carolina, Chapel Hill, on May 8, 1903, at 8.15 P.M., with Presiding Officer Chas. E. Brewer in the chair.

After the transaction of some miscellaneous business the following program was presented and discussed :

1. "A Simple Hydrogen Sulphide Apparatus," by Chas. E. Brewer.
2. "Assimilation of Free Nitrogen by Bacteria," by G. S. Fraps.
3. "Recent Progress in the Dyeing Industry," (Report) by G. S. Fraps.
4. "Nitrification in Typical North Carolina Soils," by W. A. Withers and G. S. Fraps.
5. "Rate of Nitrification of Different Fertilizers," by W. A. Withers and G. S. Fraps.
6. "Certain Derivatives of Trichlorethylidenedi-*p*-nitrophenamine," by A. S. Wheeler and M. R. Glenn.
7. "The Determination of Glycerine," by A. S. Wheeler and W. R. Weller.
8. "Mercurous Sulphide," by Charles Baskerville.
9. "Recent Investigations of the Rare Earths in the Chemical Laboratory of the University of North Carolina," by Charles Baskerville.
10. "Note on Thermodynamical Calculation of Latent Heat," by J. E. Mills.
11. "Molecular Attraction," by J. E. Mills.
12. "Some New or More or Less Novel Forms of Laboratory Apparatus :

- (a) An Unusual Form of Siphon.
- (b) A Modified Form of a Previously Described Filter-Washer.
- (c) An Automatic Measurer and Dispenser of the Acid Used in Kjeldahl Nitrogen Determinations.
- (d) Same for the Alkalies.
- (e) A Stand for Kjeldahl Digestion Flasks.
- (f) A File for Samples Contained in Bottles.
- (g) A Desiccator for Equalizing Inside and Outside Air-Pressure.

- (h) An Appliance for Utilizing the Incandescent Electric Light as Source of Heat in Fat-Extractions with Ether.
- (i) An Asbestos Furnace for Gold Assays.
- (j) An Economical but Efficient Blast-Lamp.
- (k) "Spiral Support for Round-Bottom Flasks," by J. M. Pickel.

13. "An Efficient Asbestos or Graphite Muffle," by J. M. Pickel and C. B. Williams.

Immediately upon adjournment of the Section, Dr. Charles Baskerville tendered the members and visitors a most enjoyable "smoker" at his residence.

C. B. WILLIAMS, *Secretary*.

#### COLUMBUS SECTION.

The Columbus Section held its April meeting as usual, in the Kauffman-Lattimer Building. Two papers were given, one by A. D. Cole, on "Ionization of Gases," and one by C. W. Foulk, on "Experimental Evidence Not in Harmony with the Theory of Electrolytic Dissociation."

The May meeting was held as usual in the Kauffman-Lattimer Building. Mr. E. G. Horton, chemist and bacteriologist for the Ohio State Board of Health, read a paper on "Typhoid Fever and Water Supply in Ohio." Short papers were given by W. F. Coover, on "Comparison of Methods for Standardizing Permanganate Solutions," and by M. W. Mumma, on "The Electrolytic Deposition of Bismuth."

C. W. FOULK, *Secretary*.

#### WASHINGTON SECTION.

A special meeting was held Saturday, May 2, 1903, at 8 P.M., in the Chemical Lecture Hall, Columbian University. Professor J. W. Mallet gave the address of the evening: "Applied Chemistry in the South During the Civil War, 1861-1865."

The 143d regular meeting was held Thursday, May 14, 1903, at 8 P.M., in the Assembly Hall of the Cosmos Club, 1520 H Street, N. W.

The following papers were read: "History of Petroleum Distillation," by D. J. Kelly; "Petroleum Products Used in the Paving Industry," by A. W. Dow; "Effect of Certain Acids on Clover Seedlings," by F. K. Cameron and J. F. Breazeale.

J. S. BURD, *Secretary*.

#### NORTHEASTERN SECTION.

The forty-fourth regular meeting of the Section was held at the rooms of the Technology Club, Boston, Friday, April 24th, at 8 o'clock P.M., President A. H. Gill in the chair. Seventy-five members were present.

Mr. George W. Priest addressed the Section on "The Manufacture of Chrome Leather," describing the usual method of preparing the raw hide for tanning, and the two methods used for chrome-tanning, known as the one-bath and two-bath processes. The lecturer also described the new process for making patent leather from chrome-tanned skins, and exhibited specimens of leather tanned in various ways. The address was followed by a general discussion of the subject by members interested in the tanning industry.

The forty-fifth regular meeting of the Section was held Friday, May 22nd, at 8 o'clock P.M. at the Technology Club, Boston, Vice-President Henry Howard in the chair. Thirty-five members were present.

Professor S. W. Stratton, of Washington, D. C., gave an address on "The National Bureau of Standards," in which, after an historical introduction, he described the functions of the bureau, and gave a very full description of the two buildings now being erected in the outskirts of Washington for the use of the bureau. The present work of the bureau was explained, and lantern slides showing the plans of the new buildings were shown.

ARTHUR M. COMEY, *Secretary*.

#### NEW YORK SECTION.

The eighth regular meeting of the Section was held Friday, May 8th, at 8.15 P.M., in the Assembly Hall of the Chemists' Club, 108 West 55th Street.

The program for the evening was as follows: "Cryolite, Its Mineralogy, Geology, and Technical Application," (extracts from a monograph), by I. I. Moltkehanen; "3-Nitro-phthalyl Chloride and Its Action with Ammonia and with Aromatic Amines," by V. J. Chambers; Linseed Oil (the Composition of the 'Break')," by G. W. Thompson; "The Chemistry of the Cell," by P. A. Levene.

FRANCIS D. DODGE, *Secretary*.

#### CINCINNATI SECTION.

The rooth regular meeting of the Section was held in the Ohio Mechanics' Institute, 6th and Vine Sts., Wednesday, May 13th, at 8 o'clock P.M.

The following topics for discussion were presented: "The Changes which Chemistry Has Wrought in Medicine and Surgery," by L. L. Watters; "A Method for the Detection of Chlorides, Bromides, and Iodides," by Stanley Benedict and J. F. Snell; Reviews, by Thomas Evans.

J. F. SNELL, *Secretary*.

## CHICAGO SECTION.

The May meeting of the Chicago Section was held at the rooms of the Chicago Drug Trade Club, 180 Randolph St., Wednesday May 13th, at which time a very interesting paper on "Petroleum" was read by Dr. Gray. Fifty members were in attendance.

W. A. CONVERSE, *Secretary*.

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CHEMIST FOR U. S. GEOLOGICAL SURVEY.

The Civil Service Commission will hold a competitive examination during the summer or fall to fill a position as assistant chemist in the Geological Survey, salary, \$1,200. No applicants who are unable to do independent research work in mineralogy and crystallography will be considered. Ability to do independent chemical research work, while desired, is not an essential condition, although a good knowledge of analytical chemistry is demanded. For information as to dates and places for holding the examination and subjects to be covered, applicants should address the Civil Service Commission at Washington.

It is probable that another position as assistant chemist will be open to competition in the Geological Survey during the summer. The position is one paying \$1,800 per annum. Only a fair knowledge of mineralogy will be required of applicants for it, but they must be men of experience, well versed in chemical analysis, and able to do independent work on problems relating to geology. The examination in this latter case will not be of the usual kind, but the markings will be based on education and technical experience, a thesis of a thousand words, and published work. As the filling of this position is not yet in the hands of the Civil Service Commission, inquiries and addresses should be sent to the director of the Geological Survey, at Washington.

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WARNING.

Within the last four months, an individual well acquainted with the conditions of chemical laboratories of manufacturing plants, especially iron and steel works, is plundering the chemical laboratories in Virginia, West Virginia, and now Ohio, of their platinum ware. Over a dozen of such laboratories have been reported within the last four months, and from the way the thief goes about it, it is evident that he must have been a former iron chemist, thoroughly acquainted with the conditions of the chemical laboratories in the district mentioned. From what we learn, he is now traveling up the Ohio River, toward Pennsylvania, and chemists of iron, cement, and steel works, etc., throughout central United States, should be on their guard against him.

## Proceedings.

### COUNCIL.

#### MEMBERS ELECTED BETWEEN MAY 21, AND JUNE 30.

Arnold, William H., 135 Adams St., Chicago, Ill.  
Baldwin, F. H., Bayonne, N. J.  
Brown, William D., 7047 Hamilton Ave., Pittsburg, Pa.  
Clarke, Simeon, Gorham, N. H.  
Eaton, Edward M., Latrobe, Pa.  
Edwards, John E., Sewickley, Pa.  
Fink, Colin G., 133 W. 85th St., New York.  
Hoy, John F., "The Glyndon," Bellevue, Pa.  
Hunnings, S. V., American Locomotive Works, Allegheny, Pa.  
Jones, J. Shirley, Stiles Hall, Berkeley, Pa.  
Machalske, Florentine J., Box 25, Sta. W., Brooklyn, N. Y.  
McClester, Thomas Frank, 121 Walter Ave., Pittsburg, Pa.  
Miller, Joseph J., 6728 Hamilton Ave., Pittsburg, Pa.  
Northrup, J. C., 208 4th Ave., Homestead, Pa.  
Ogden, J. Bergen, 262 Fifth Ave., New York.  
Redfern, E. L., 246 N. 17th St., Lincoln, Neb.  
Schwartz, H. A., 3335 W. Michigan St., Indianapolis, Ind.  
Snyder, Charles G., Rodgers and Orchard Aves., Bellevue, Pa.  
Steel, J. C. H., 217 Sansome St., San Francisco, Cal.  
Wigglesworth, Henry, 25 Broad St., New York.  
Wright, Paul Duffield, 1214 Buena Vista St., Allegheny, Pa.

#### CHANGES OF ADDRESS.

Baxter, Albert C., Ashland, Ill.  
Diehl, Oscar C., Saginaw Salt Co., St. Charles, Mich.  
Elliott, Edward C., Teachers' College, Columbia Univ., New York, N. Y.  
Ferrero, Felice, 1322 Washington St., San Francisco, Cal.

Fink, Colin G., care of Eisenbahndirektor Carl Fink, Hanover, Germany.

Freskow, Fritz, Saginaw, Mich.

Fuller, Henry C., 83 N. Washington St., Boston, Mass.

Hill, Arthur E., 118 Mt. Pleasant Ave., Newark, N. J.

Kennedy, M. B., Alpena, Mich.

Mabery, C. F., North Gorham, Me.

Mayer, Andrew, Jr., care of Carnegie Steel Co., Edgar Thompson Works, Braddock, Pa.

Merrigold, Benjamin S., Collegiate Dept., Clark Univ., Worcester, Mass.

Mueller, Max E., 221 Pine Grove Ave., Chicago, Ill.

Murrill, Paul, Woodbury, N. J.

O'Neill, J. G., care of Cayuga Lake Cement Co., Ithaca, N. Y.

Reiderer, Emil J., care of Forcite Powder Co., Landing P. O., N. J.

Ricketts, P. DeP., 104 John St., New York, N. Y.

Ross, Samuel H., Cor. 23rd and K Sts., So. Omaha, Neb.

Schade, James W., 238 Hazen St., Ithaca, N. Y.

Sherman, Geo. W., Akron, O.

Smither, F. W., 310½ Union St., Nashville, Tenn.

Thompson, Firman, Sugar City, Colo.

Thompson, John F., Georgetown, Sagadahoc Co., Maine.

Wells, J. Walter, 392 Markham St., Toronto, Can.

Wingate, Hamilton, 24 Wynell Road, Forest Hill, London.

Worrell, Steve H., Box 154 University Sta., Austin, Texas.

**DECEASED MEMBER.**

Dr. Albert H. Chester, of New Brunswick, N. J., member of the Society since 1876, died April 13, 1903.

**MEETINGS OF THE SECTIONS.**

**NEW YORK SECTION.**

The annual meeting was held on June 5th, at the Chemists' Club, 108 West 55th Street. The program was as follows: "The Preparation of Anisic Acid from Oil Anise," by Carl H. Zieme and M. T. Bogert; "The Influence of Atmospheric Oxidation upon the Composition and Analytical Constants of Fatty Oils" (in abstract), by H. C. Sherman and M. J. Falk; "A Rapid Method



for the Determination of Arsenic in Arsenopyrite" (in abstract), by J. L. Danziger and W. H. Buckhout; "On the Structure of Metals and Alloys" (Part III), by Wm. Campbell—read by title; "On the Chemistry of the Cell," by P. A. Levene.

The election of officers was then held. Edmund H. Miller was chosen chairman and Francis D. Dodge, secretary.

FRANCIS D. DODGE, *Secretary*.

#### KANSAS CITY SECTION.

Since last reported, the Kansas City Section has held the following meetings: The 15th meeting was held at Lawrence, Kas., October 16, 1902, in connection with the dedication of the Chemical Building of the University of Kansas. The papers presented were: "The Rôle of Chemistry in Higher Education," by Dr. Harvey W. Wiley; "A New Reaction of the Formamidines," by F. B. Dains; "Ionic Velocities in Liquid Ammonia," by E. C. Franklin.

The 16th meeting was held at Kansas City, November 11, 1902. Subject of paper, "The Manufacture and Chemistry of Glass," by A. R. Miller.

The 17th meeting was held at Kansas City, December 13, 1902. Subject of paper, "The Structure of Camphor," by R. C. Warren. The election of officers resulted in a reelection of all officers.

The 18th meeting was held at Kansas City, January 10, 1903. Subject of paper, "The Distillation of Coal Tar," by W. H. Fulweiler.

The 19th meeting was held at Kansas City, February 14, 1903. Subject of paper, "Crackers," by L. L. Cayvan.

The 20th meeting was held at Kansas City, March 14, 1903. Subject of paper, "Kansas Petroleum," by E. C. Bartow.

The 21st meeting was held at Iola, Kas., April 11, 1903. The time was spent in visiting the plants of the Iola Portland Cement Company, the United Zinc and Chemical Company, The Cherokee-Lanyon Spelter Company and the Zinc Rolling Mills. Dr. Oscar Gerlach entertained the Society at dinner.

The 22nd meeting was held at Lawrence, Kas., May 9, 1903. Subjects of papers, "Some Experiments with Matter at Low Temperatures," by H. P. Cady; "Catalysis" (illustrated by experiments), by E. C. Franklin.

The Section adjourned until October, 1903.

ARMAND R. MILLER, *Secretary*.

## NEBRASKA SECTION.

The 32nd regular meeting of the Nebraska Section was held in the Chemical Laboratory of the University of Nebraska, Saturday, June 6, 1903, at 8 P.M. The following papers were read: "Recent Volumetric Methods for the Estimation of Arsenic in Insecticides," by Dr. Samuel Avery; "A New Class of Double Lead Salts," by Dr. John White.

JOHN WHITE, *Secretary*.

## CINCINNATI SECTION.

The 102nd regular meeting of the Section was held in Hanna Hall, University of Cincinnati, Wednesday, June 10th, at 8 P.M. The following topic for discussion was presented: "Recent Additions to Our Knowledge of the Chemistry of the Metals of the Platinum Group," by James Lewis Howe.

J. F. SNELL, *Secretary*.

## RHODE ISLAND SECTION.

At the regular meeting held March 27th, Dr. H. W. Wiley was the guest of the Section, and a dinner was given in his honor.

No meeting was held in April.

At the meeting held May 21st, Mr. Charles E. Swett addressed the Section on "The Treatment of the Waste Waters of a Woolen Mill."

CHAR. M. PERRY, *Secretary*.

## CALIFORNIA SECTION.

The eleventh meeting of this Section was held Saturday, May 9th, at 8 P.M., in Jules Restaurant, 315 Pine Street, San Francisco, and the paper of the evening was by Professor W. B. Rising, of the University of California, on "Development of Chemical Industry in Germany."

HARRY EAST MILLER, *Secretary*.

## PITTSBURG SECTION.

The third regular monthly meeting of the Pittsburg Section of the American Chemical Society was held with the Chemical Section of the Engineers' Society of Western Pennsylvania, at their rooms, No. 410 Penn Avenue, Thursday evening, May 21, 1903.

A paper was read by Mr. J. E. Babb, on "Methods of Analysis and Data on the Composition of Aqua Regia."

GEO. P. MAURY, *Secretary*.

## CORNELL SECTION.

The fourth regular meeting of the Cornell Section was held in Chemical Lecture Room No. 1, on Monday May 18th, at 8.00 P.M.

Professor Ernest Merritt, of the Department of Physics, addressed the Section on "Some Recent Development in the Study of Radioactive Substances."

W. C. GIER, *Secretary*.

## MICHIGAN SECTION.

A meeting was held on Friday, March 27th, at the University of Michigan. The following papers were presented: G. O. Higley, "Some Hydrates of Chromium Chloride;" A. N. Clover, "Hydrolysis of Organic Peroxides;" P. F. Trowbridge, "The Recovery of Sugar from Beet Molasses." The following officers were reelected for the ensuing year: *President*, E. D. Campbell; *Councilor*, M. Gomberg; *Secretary-Treasurer*, Alfred H. White; *Elective Members of the Executive Committee*, P. F. Trowbridge, S. G. Jenks, O. Button.

ALFRED H. WHITE, *Secretary*.

## CONGRESS OF APPLIED CHEMISTRY.

I beg to offer, herewith, the report of the committee appointed by the president of the Society, under the authority of the Council, to organize the American sections of the Fifth International Congress of Applied Chemistry which met in Berlin, Germany, June 2-8, 1903.

The names of the members of the committee appointed are found in the Journal of the Society, Vol. XXIV, No. 12, Proceedings, pages 91-94.

Since the publication of the list, the Chairman of Section IX, Dr. L. H. Friedburg, requested that he be relieved of his duties as chairman on account of private business, and Dr. Leo Baekeland, of Snug Rock, Yonkers, N. Y., was appointed in his place.

The chairman of each of the sectional committees was requested to undertake all the work in connection with his particular section and the other members of the sectional committees were requested to collaborate with him. This subdivision of the work resulted most happily both in respect of securing the interest of the members of the Society in the Congress, and especially in obtaining large numbers of papers for transmission to Berlin.

The response of American chemists to the appeals of the chairmen of the various sections was most generous. The members were given the option of either sending their membership fees directly to Berlin or of transmitting them to the Chairman of the General Committee. Through the latter source there have been forwarded to Berlin 122 membership fees, for which receipts are held. Your chairman has no means of knowing how many membership fees were forwarded directly to Berlin or paid there on the arrival of delegates from this country. There is every reason to

believe, however, from the knowledge at hand, that the total membership from this county will reach nearly 150.

The Chairman of the General Committee also undertook to distribute the invitations to American chemists, and of these there were 1200 sent, only a little more than half enough to send to the members of our Society. These were distributed to such members as it was thought would be most interested in the Congress. The general invitation, however, in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY for December, 1902, was of such a character as to bring to the attention of the members the general purpose and scope of the Congress.

An official invitation from the German Government to the Government of the United States to participate in the Congress came too late to insert in the Journal. Under this invitation, the Secretary of the State, when furnished with the proper recommendations, appointed a number of the members of the Society as delegates from the United States. The president of the Society also gave, under the authority of the Council, special certificates to members of the Society who expected to be present in person. Five certificates of a similar character were issued by the president of the Electrochemical Society. Your chairman is not in possession of all the data in the case, but from correspondence and personal interviews he believes there were from twenty-five to thirty delegates present at Berlin from this country. He regrets that official business of an imperative character prevented him from joining them at the Congress.

The number of papers received by the chairman of the Committee for transmission to Berlin was 99. As doubtless many papers have been sent directly to Berlin by their authors and are not included in this list of papers forwarded from this country, the total number will certainly be more than 100.

The titles and authors of these papers follow:

"Miscellaneous Methods of Inorganic Analysis and Assay (except Electrolytic Methods and those pertaining to the Rare Earths)," W. F. Hillebrand.

"Rare Earths," Chas. Baskerville.

"Electrochemical Analysis," F. J. Moore.

"Mineral Chemistry," W. F. Hillebrand.

"Methods Used in Alkali Works," J. D. Pennock and D. A. Morton.

"Iron and Steel," A. A. Blair.

"Portland Cement," C. Richardson.

- "Explosives," C. E. Munroe.
- "Sanitary Chemistry (Water, Air)," Mrs. E. H. Richards.
- "Fertilizers," F. P. Veitch.
- "Ultimate Organic Analysis," H. W. Hillyer.
- "American Practice in the Examination of Petroleum and Petroleum Products," S. S. Sadtler.
- "Bitumens," C. Richardson.
- "Oils (except those used for Paints), Fats, Soaps," A. H. Gill.
- "Pharmaceutical Chemistry," L. F. Kebler.
- "Ash Ingredients of Plants," G. S. Fraps.
- "Tanning," W. H. Krug.
- "Dairy Products and their Substitutes," G. E. Patrick.
- "Human Foods," W. D. Bigelow.
- "Sugars," L. S. Munson.
- "Cattle Foods," J. K. Haywood.
- "Insecticides and Fungicides," J. K. Haywood.
- "Addenda—Combustion and Other Heating Apparatus," W. F. Hillebrand.
- "Drawing of Samples and Analyzing Carbide and Acetylene," J. M. Morehead.
- "Boric Acid and Borax," Edward Hart.
- "Sulphuric Acid—Review of the Progress in the United States since 1900," F. J. Falding.
- "Progress of the Soda Industry in the United States since 1900," J. D. Pennock.
- "Development in the Carborundum and Graphite Industries since 1900," E. G. Acheson.
- "Mixed Acids for Nitrocellulose Manufacture," G. W. Patterson.
- "Regulations for Transportation of Explosives," Penn. R.R. Co.
- "Some Chemical Constants of Fossil Resins," R. A. Worstall.
- "A Preliminary Report upon the Oxidation of Linseed Oil," F. L. Dunlap and F. D. Shenk.
- "On the Occurrence of Cholesterol in Olive Oil," A. H. Gill and A. G. Tufts.
- "Review of the Progress in Organic and Technical Chemistry Relating to Forest Products in the United States from July, 1900, to the Present Time," W. H. Krug.
- "The Present Status of the Extract Industry in the United States, 1903," G. A. Kerr.
- "The Wood Distillation Industry in the United States in 1900," C. E. Munroe.
- "Waste Waters from Pulp and Paper Mills," M. L. Griffin.
- "The Development of the By-Product Coking Industry in the United States," E. W. Parker.
- "By-Product Coke Industry of the United States," J. D. Pennock.
- "Corn Oil—Its Manufacture and Chemical Properties," Thos. Gaunt.
- "The Present Status of the Dyeing Industries of the United States," J. M. Matthews.

- "The Coal-tar Industry in the United States," H. W. Jayne.
- "The Cellulose Industries in the United States," A. D. Little.
- "The Commercial Utilization of Milk Waste and the More Recent Products of Milk in a Dry Form," J. A. Just.
- "Some Metabolism Experiments in Poultry," E. A. de Schweinitz and E. W. Brown.
- "The Composition of the Tubercle Bacilli from Various Animals," E. A. de Schweinitz and M. Dorset.
- "Notes on Testing Soils for Application of Commercial Fertilizers," H. A. Weber.
- "The Services of Chemistry and Allied Sciences Applied to Agriculture in the United States," H. W. Wiley.
- "A New Method for Performing Metabolism Experiments," F. H. McCrudden.
- "Nutrition Investigations in California," M. E. Jaffa.
- "Investigations on the Nutrition of Man Conducted under Supervision of the Office of Experiment Stations, U. S. Department of Agriculture," R. D. Milner.
- "Drugs and Their Adulterations and the Laws Relating Thereto," H. W. Wiley.
- "Résumé of Japanese Nutrition Investigations," K. Oshima.
- "On the Toning Action of a Mixture of Thiosulphate of Sodium and Alum," Leo Baekeland.
- "Method for Determining the Relative Permanency of Photographic Prints," Leo Baekeland.
- "The Photochemical Industry of the United States," Leo Baekeland.
- "On the Influence of Hygrometric Conditions of the Atmosphere in the Manufacture of Photographic Paper," Leo Baekeland.
- "Photo-retrogression, or the Disappearance of the Latent Photographic Image," Leo Baekeland.
- "Centrifugal Bromide of Silver for Bromide Emulsions," Leo Baekeland."
- "The Art and Science of Silvering Mirrors," M. Toch.
- "A Practical Method for the Quantitative Determination of Silver in Photographic Paper," Leo Baekeland.
- "The Electrolytic Action of Metallic Particles in Sensitized Papers," Leo Baekeland.
- "Report on the Progress in Electrochemistry in the United States since 1900," C. A. Doremus.
- "Outline of Researches in Physical Chemistry Made in America," A. A. Noyes and W. D. Bancroft.
- "Legal and Economic Problems in Connection with the Chemical Industries," J. W. Mallet.
- "Food Legislation in the United States," W. D. Bigelow and H. W. Wiley.
- "Report of the Committee on Mining, Metallurgy and Explosives in the United States," C. E. Munroe.

"On the Presence and Effect of Ferric Oxide, on Commercial Hop Extracts," C. B. Davis.

"On the Manufacture of Ferro-titanium and Other Metallic Alloys Electrically," A. J. Rossi.

"A Process for the Treatment and Utilization of Fine Dust, Down-comer Dust, Stove Dust, and Fine or Mesaba Ores, in the Blast-furnace," J. C. Attix.

"Progress of Chemistry in the Leather Trade," E. D. Deming.

"Recent Progress in the Salt Industry in the United States of America," E. H. S. Bailey.

"The Cement Industry in the United States," E. B. McCready.

"Liquid Air," E. C. Foster.

"The Pittsburg Coal Seam," F. Z. Schellenberg.

"A New Centrifugal Soil Elutriator," P. A. Yoder.

"Nitrification in Arable Soils," W. A. Withers and G. S. Fraps.

"Determination of the Nitrifying Power of Soils," G. S. Fraps.

"The Analysis of Wheat and Flour for Commercial Purposes," Harry Snyder.

"Methods for the Determination of Total Phosphoric Acid and Potash in Soils," C. B. Williams.

"Fertilizers," J. P. Street.

"A Review of the Progress in Chemistry of Insecticides and Fungicides since July 1, 1900," J. K. Haywood.

"A Résumé of Some Chemical Studies upon Soils, Made in America, 1900-1903," F. K. Cameron.

"Abstracts Relating to Apparatus Employed in Agricultural Chemical Analysis, July, 1900, to April, 1903," B. B. Ross.

"Feedstuffs: Their Analysis, Composition, Digestibility, Sophistication, Manufacture, and Value for Specific Purposes," C. F. Langworthy.

"Review of the Condition of the Chemical Industries of Organic Products in the United States," Wm. McMurtrie.

"Carbon Blacks," G. L. Cabot.

"A Method of Qualitative Analysis for All the Elements Precipitable by Hydrogen Sulphide," A. A. Noyes.

"The Estimation of Formaldehyde in Milk," B. H. Smith.

"A Comparative Study of Methods of Determining Formaldehyde," B. H. Smith.

"A Study in Raffinose Determinations," D. L. Davoll.

"The Influence of Environment on the Composition of the Sugar-Beet," H. W. Wiley.

"The Permissible Quantity of Sugar in Imported Preserved Bananas,"

H. W. Wiley.

"The Composition of Fresh and Canned Bananas," L. S. Munson and L. M. Tolman.

Some of the papers arrived here too late to reach Berlin in time to print before the beginning of the Congress, and therefore I have not had a receipt from Dr. George Pulvermacher, the general

secretary, of their arrival in Berlin. I have, however, his receipt for the arrival of eighty-one papers, some of which reached him in time to be printed before the Congress began; the others, unless some unusual delay occurred in the mails, arrived in time to be presented to the Congress. The papers were assigned to the following sections:

Section I, 30 papers; Section II, 8 papers; Section III, 3 papers; Section IV, 18 papers; Section V, 4 papers; Section VI, 0 papers; Section VII, 17 papers; Section VIII, 5 papers; Section IX, 9 papers; Section X, 3 papers; Section XI, 2 papers.

The average number of typewritten pages per paper was 10, making the total number of typewritten pages forwarded to Berlin 990. It can be seen from the above assignment of papers that every section is represented by one or more papers except Section VI.

Dr. Pulvermacher, in acknowledging the receipt of the papers, informed me that the Committee on Publication had decided to publish no papers in the proceedings unless the authors were members of the Congress. Twenty-five of the authors of papers, at the time Dr. Pulvermacher acknowledged their receipt, had not qualified as members of the Congress. I immediately addressed a note to each of these authors, asking him to forward at once directly to Dr. Pulvermacher the membership fee of 20 marks, in order that his paper might appear in the published proceedings. The collection of these large amounts of original valuable material from the American chemists is due especially to the chairmen of the various sections, who, by personal correspondence and otherwise, were able to present so many papers on the respective subjects assigned to them.

H. W. WILEY,

*Chairman of the American  
Committee on Organization.*



## Proceedings.

### MINUTES OF THE TWENTY-EIGHTH GENERAL MEETING OF THE AMERICAN CHEMICAL SOCIETY.

The twenty-eighth general meeting of the American Chemical Society was held at Cleveland, Ohio, June 29 and 30, 1903.

The opening session was held at the rooms of the Associated Technical Clubs, at 9.30 A.M., Monday, June 29th. Professor Edward W. Morley gave a brief address of welcome in behalf of the Cleveland Chemical Society, and there was a reply by President John H. Long.

The following papers were presented.

"Contributions to the Chemistry of Hydronitric Acid," by L. M. Dennis and A. W. Browne.

"The Transport Number of Sulphuric Acid," by O. F. Tower.

"The Rôle of Water in the Electro-Deposition of Lithium from Pyridine and from Acetone," by H. E. Patten and W. R. Mott.

"The Viscosity of Solutions of Metallic Salts: Its Bearing upon the Nature of the Compound between Solvent and Solute," by Arthur A. Blanchard.

"The Constitution of Sulphur Chloride," by W. R. Smith and I. F. B. Wade.

"Mercurous Sulphide," by Charles Baskerville.

"The Proportions of Silver Nitrate and of Silver Sulphate Formed by the Action of Nitric Acid on Silver Sulphide," by Hippolyte Gruener.

"The Action of Dissolved Oxygen on Cuprous Chloride," by W. M. Blanchard and Bert D. Ingles.

"The Action of Hydrogen Peroxide on Cuprous Chloride," by W. M. Blanchard.

"On the Changeable Hydrolytic Equilibrium of Dissolved Chromic Sulphate," by T. W. Richards and F. Bonnet, Jr.

Monday afternoon, members of the Society were taken on a drive, which gave a view of one of the chief industrial centers of Cleveland, and included the following special features: Cleveland Furnace Company, Central furnaces, River Furnace, Grasselli Chemical Company, Standard Oil Company, and many minor industrial concerns. The viaducts and bridges, and the complete dock system of Cleveland. Dry dock, ore docks, and automatic unloaders. Ship yards.

Monday evening, Dr. Gomberg gave a lecture at the University Club on the subject of "Trivalent Carbon." This was followed by a social meeting under the auspices of the Cleveland Chemical Society.

Tuesday morning, June 30th, a session was held in the lecture room of the Chemical Laboratory of the Case School of Applied Science. The following papers were presented:

"2-Amino-3,5-bibrombenzoic Acid, Its Nitrile, and Synthesis of Quinazolines from the Latter," by Marston T. Bogert and William F. Hand.

"The Acids of the Colophonium of the Northern Pine," by G. B. Frankforter and Clara Hillsheim.

"The Products of the Pitch of the Douglass Fir," by G. B. Frankforter.

"The Derivations of Eugenol," by G. B. Frankforter and Max Lands.

"The Synthesis of  $\beta$ -Methyladipic Acid," by W. A. Noyes and I. J. Cox.

"Kansas Petroleum," by Edward Bartow.

"The Determination of Sulphur in Iron," by Allen P. Ford and Ogden G. Willey.

"The Toxic Limits of Acid for Some Seedlings," by Frank K. Cameron.

"Analysis of Sea-Water from Wood's Hole, Mass.," by A. P. Saunders.

"On the Relation of the Specific Gravity of Urine to the Solids Present," by J. H. Long.

"Cereal Foods," by Edward Gudeman.

"The Determination of Starch," by W. A. Noyes and R. B. Arnold.

A very hearty vote of thanks was given to the Cleveland Chemical Society for the very excellent arrangements made for the entertainment of the Society; to the Associated Technical Clubs of Cleveland; to the University Club; to the Case School of Applied Science; to Mr. Hippolyte Gruener for the excellent manner in which he carried out the wishes of the Cleveland Chemical Society in making the arrangements for the meeting; and to the Grasselli Chemical Company for the drive through the parks of Cleveland and the luncheon at the Hollenden, which they so generously provided. The formal meeting was then adjourned.

After the morning session, the members of the Society were entertained by a drive through the Cleveland parks and a luncheon, by courtesy of the Grasselli Chemical Company.

Tuesday afternoon there was the alternative of two excursions: (1) Newburg Rolling Mills, blast-furnaces, Bessemer converters, Wellman-Seaver open-hearth furnaces, and rolling mills. (2) Gas Works, No. 2, coal and water gas plants, and United Salt Company (salt from brine wells).

Tuesday evening, at 7 o'clock there was an informal subscription dinner at the Hollenden Hotel. President Long acted as toastmaster and there were responses by Messrs. Mabery, Prescott, Ross, Frankforter, Barton, Dennis, W. R. Smith, Pond and Cameron.

Wednesday morning, a few of the members visited the plant of the Cleveland Furnace Company.

#### BOARD OF DIRECTORS.

A meeting of the Board of Directors was held at the Chemists' Club, 108 W. 55th St., New York City, July 9, 1903. The directors present were A. P. Hallock, C. A. Doremus, E. E. Smith and W. A. Noyes. In the absence of the president, A. P. Hallock was chosen chairman, *pro tem*.

It was moved that all action and recommendations of the Council taken at the Washington and Cleveland meetings, so far as these pertain to finance or to business of the Society which comes legitimately before the Directors, are hereby adopted and approved by the Directors.

It was moved that the duplicate key of the safe deposit vault be entrusted to the chairman of the Finance Committee. This chairman is now Mr. I. H. Wainwright.

It was moved that the treasurer's bond be entrusted to the chairman of the Finance Committee, Mr. J. H. Wainwright, and that the stock certificate and everything else representing the invested funds for the endowment of the Nichols Prize Medal for the New York Section, be entrusted to the treasurer.

WILLIAM A. NOYES, *Secretary*.

### COUNCIL.

The Council met at the University Club, Cleveland, Ohio, at 7.45 P.M., June 29, 1903. There were present Messrs. Long, Morley, J. W. Richards, Evans, Cameron, Converse, Gudeman, Parsons, Talbot, McPherson, Dennis, and W. A. Noyes. President J. H. Long was in the chair.

Professor Morley presented, for the Committee on Coöperation with the National Bureau of Standards, a preliminary draft of regulations for apparatus to be used in volumetric chemical analysis. It was moved that the report be referred back to the committee and that the latter be authorized to amend the same and publish their report with the authority of the Society.

Professor Morley moved that the winter meeting of the Society be held at St. Louis in conjunction with the meeting of the American Association for the Advancement of Science.

Professor Talbot presented an informal report for the Committee on the Quality of Chemical Reagents.

Professor Talbot moved to recommend that an appropriation of \$100 be made by the Directors, to be expended by the editor in securing reports of recent progress in various fields of chemistry.

Dr. Cameron moved that the report of the Committee on Organizing Divisions of the Society be received and the committee discharged. It was then moved that the same committee be reappointed and requested to formulate a less radical plan for the promotion of the interest of the members of the Society in its meetings, after consideration of the ideas expressed in the communications from the various members of the Council. The meeting was then adjourned.

W. A. NOYES, *Secretary*

### MEMBERS ELECTED BETWEEN JUNE 20 AND JULY 20.

Arney, H. V., 356 Superior St., Cleveland, O.

Curtiss, Richard Sydney, Union College, Schenectady, N. Y.

Koch, Julius A., School of Pharmacy, Pittsburg, Pa.

Spencer, John G., 261 Amesbury Ave., Cleveland, O.

Zieme, Carl H., 308 Sherman Ave., Jersey City Heights, N. J.

CHANGES OF ADDRESS.

Bartow, Edward, Douglas, Mich.

Bourne, Lyman F., The Abbott House, Old Orchard, Me.

Felt, W. W., Golden, Colo.

Franklin, Edward C., Stanford University, Cal.

Glasoe, P. M., Spring Grove, Minn.

Hall, Roy D., U. of P. Dormitories, West Philadelphia, Pa.

Hancock, Thomas J., Fruitport, Mich.

Harms, Armin, care of Compania Metallurgica Mexicana, San Luis Potosi, Mex.

Harrell, George R., Copperfield, Vt.

Herreshoff, J. B. F., 40 W. 69th St., N. Y. City.

Hill, Lucien A., Asst. Chemist, McLean Hospital, Waverly, Mass.

Johnson, E. M., Box 163, Gas, Kans.

Kohr, D. A., 43 Wrol Ave., Dayton, Ohio.

Lawson, William L., Garland, Utah.

Lenk, Walter S., care Lenk Wine Co., Toledo, Ohio.

Lyon, Alberto C., 921 N. Center St., Terre Haute, Ind.

Makayama, Takakichi, care Forest Paper Co., Yarmouthville, Me.

Mojonnier, Timothy, care Helvetia Milk Condensing Co., Greenville, Ill.

Myers, Rolin G., care Struthers Furnace, Struthers, O.

O'Connell, C. J., Lakota, N. D.

Palmer, Irving A., Eilers Plant, A. S. & R. Co., Pueblo, Colo.

Patterson, Austin M., care G. & C. Merriam Co., Springfield, Mass.

Porter, John Lewis, 602 Carondelet St., New Orleans, La.

Prentiss, Geo. N., 2910 Clybourn St., Milwaukee, Wis.

Riederer, Herman S., Newton, Sussex Co., N. J.

Russell, Lee, 1 Normal St., Worcester, Mass.

Rust, R. R., Mineral Point Zinc Co., North Chicago, Ill.

Sy, Albert P., Sandy Hook Proving Ground, Port Hancock, N. J.

Thurlow, Nathaniel, Port Chester Chem. Co., Port Chester, N. Y.

Tibbals, C. A., Jr., Marlboro-on-Hudson, N. Y.

Van Gelder, A. P., Emporium, Pa.  
Warville, F. G., 66 Rush St., Flat No. 15, Chicago, Ill.  
Weber, R. F., Salamanca, N. Y.  
Wheeler, F. G., Wyandotte, Mich.  
Winter, Frank C., Stanford University, Cal.  
Wolcott, Clifford H., Spring Valley, Wis.

**ADDRESSES WANTED.**

DuPont, F. G., formerly Montclair, N. J.  
Myers, Ralph E., formerly 130 S. South College St., Columbus,  
Ohio.  
Perri, Mali, formerly 8 5th Ave., N. Y. City.

**MEETINGS OF THE SECTIONS.**

**RHODE ISLAND SECTION.**

At the regular meeting of the Rhode Island Section held June 18th, Mr. W. E. Smith read a paper on "The Manufacture of Sulphuric Acid by the Contact Process."

The following officers of the Section were reelected for the ensuing year: *Presiding Officer*, Walter E. Smith; *Secretary-Treasurer*, Chas. M. Perry; *Member of Executive Committee*, Chas. E. Swett.

CHAS. M. PERRY, *Secretary*.

## Proceedings.

### COUNCIL.

#### MEMBERS ELECTED BETWEEN JULY 20 AND AUGUST 20.

Bridge, Arthur, 657 37th Place, Chicago, Ill.  
Bryan, Guy, Jr., care N. K. Fairbank Co., St. Louis, Mo.  
Cox, J. Malcom, 717 W. Harrison St., Chicago, Ill.  
Foss, Wilfred C., Greenville, N. H.  
Gibbs, Harry Drake, Corvallis, Ore.  
Green, R. B., Eveleth, Minn.  
Isenberg, J. E., 424 N. 19th St., Philadelphia, Pa.  
Jepsen, John, 657 37th Place, Chicago, Ill.  
Johnson, Walter E., 4803 Evans Ave., Chicago, Ill.  
Kempte, Heinrich A., 182-184 Front St., N. Y. City.  
Luckie, R. Ross, Eveleth, Minn.  
Macdonald, (Miss) Margaret B., State Normal School, Trenton,  
N. J.  
Philipp, Herbert, Wyandotte, Mich.  
Scherubel, Erwin F., 5531 Kimbark Ave., Chicago, Ill.  
Schorr, Robert, 424 O'Farrell St., San Francisco, Cal.  
Slimmer, Max Darwin, care of the S. and S. Co., 41st St. to  
Ashland Ave., Chicago, Ill.  
Vollertsen, John J., 691 N. Maplewood Ave., Chicago, Ill.  
Yockey, Harry, 7th and Freeman Ave., Cincinnati, O.

#### CHANGES OF ADDRESS.

Apfel, Philip F., 315 N. 53rd Ave., Chicago, Ill.  
Arnold, Fred N., Jr., 61 Ringold St., Dayton, O.  
Arnold, Lawrence L., Balla, Pa.  
Arnold, Robert B., 308-309 Illinois Life Bldg., Louisville, Ky.  
Bennett, Hugh H., 302 N. High St., Nashville, Tenn.  
Blum, William, Univ. of Utah, Salt Lake City, Utah.  
Brinton, C. S., 335 Dean St., West Chester, Pa.  
Burd, John S., Univ. of Idaho, Moscow, Idaho.  
Clarke, C. H., Sudbury, Ont.  
Cox, Irving J., care Armour Packing Co., Kansas City, Kans.  
Craig, A. G., 217 W. 123rd St., N. Y. City.  
Dailey, J. Glanding, Apartado 84, Torreon, Coahuila, Mexico.

- Exner, Franz F., Carleton College, Northfield, Minn.  
Field, Charles, 3d, 106 College Ave., West Somerville, Mass.  
Franklin, Frederick H., 184 Whittier Ave., Providence, R. I.  
Fraps, G. S., College Station, Texas.  
Gallup, H. W., 186 Laurel Hill Ave., Norwich, Conn.  
Hart, Walter H., 2010 Wallace St., Philadelphia, Pa.  
Higgins, Francis W., care The Carborundum Co., Niagara Falls, N. Y.  
Hinckley, J. F., 1125 Park Place, Brooklyn, N. Y.  
Holland, Hazel, care of Welsbach Light Co., Gloucester City, N. J.  
Horn, A. C., Box 797, Binghamton, N. Y.  
Johnson, Charles W., Box 114, Univ. Sta., Seattle, Wash.  
Kofoid, R. N., 418 Riverside, Niagara Falls, N. Y.  
Lanning, John G., Clairton, Pa.  
Laudig, O. O., 6440 Minerva Ave., Chicago, Ill.  
Leavenworth, W. S., Olivet College, Olivet, Mich.  
McCabe, Charles R., Barberton Inn, Barberton, O.  
McCulloch, John E., 118 S. Forest Ave., River Forest, Oak Park, Ill.  
Nelson, E. K., Care of Nelson Morris & Co., U. S. Yards, Chicago, Ill.  
Palmer, Charles S., Anaconda, Mont.  
Patterson, Austin M., 57 Clarendon St., Springfield, Mass.  
Pitman, J., San Antonio Arsenal, San Antonio, Tex.  
Porter, Horace C., care of The Solvay Process Co., Syracuse, N. Y.  
Robb, John W., 499 La Salle Ave., Chicago, Ill.  
Rogers, Allen, 4627 Paschall Ave., Philadelphia, Pa.  
Root, Wm. L., 11 Church St., Pittsfield, Mass.  
Shuler, D. P., Mine LaMotte, Mo.  
Spurlin, O. L., Chemist, Georgia Cotton Oil Co., 919 Austell Bldg., Atlanta, Ga.  
Sundahl, S. A., 9035 Superior Ave., Chicago, Ill.  
Tolman, L. M., 1630 6th St., N. W., Washington, D. C.  
Volney, C. W., 173 West 81st St., New York City.  
Waldbott, Sigmund, care Ohio Mechanics Inst., 6th and Vine Sts., Cincinnati, O.  
Zimmele, H. B., 59 N. 11th St., Newark, N. J.

ADDRESSES WANTED.

- Franklin, Arthur, formerly Pullman, Chicago, Ill.  
Myers, Ralph E., formerly 130 S. College St., Columbus, O.



## Proceedings.

### COUNCIL.

#### MEMBERS ELECTED BETWEEN AUGUST 20 AND SEPTEMBER 25.

Andrews, William Henry, Care Pratt & Lamhut, Buffalo, N. Y.  
Bjorkland, Alfred, Alta, Iowa.  
Culmer, Harry H., 6200 Madison Ave., Chicago, Ill.  
Harrison, Harris D., Canyon Creek, Mont.  
Hasson, Harry, The Armour Fertilizer Works, Atlanta, Ga.  
Johnson, William, 2421 Dearborn St., Chicago, Ill.  
Nagel, Oskar, 90 Wall St., New York City.  
Steele, Wade H., Butte, Mont.  
Wessell, J. F., Box 15, Eveleth, Minn.

#### CHANGES OF ADDRESS.

Ashley, Harrison E., 1089 Acushnet Ave., New Bedford, Mass.  
Beans, H. T., Columbia University, New York City  
Berkeley, W. N., Box 446, San Juan, Puerto, Rico.  
Blanchard, Arthur A., Mass. Inst. Tech., Boston, Mass.  
Booth, William M., 601 Dillaye Bldg., Syracuse, N. Y.  
Boroschek, Leopold, 315 Greenpoint Ave., Brooklyn, N. Y.  
Bourne, L. M., Mass. Inst. Tech., Boston, Mass.  
Brown, H. E., 203 Park Ave., New Castle, Pa.  
Chambliss, Hardee, 127 Maple Ave., Flushing, N. Y.  
Clarke, C. H., Cornwall Hotel, Sault Ste. Marie, Can.  
Colby, Albert Ladd, International Nickel Co., 74 Broadway,  
New York City.  
Crane, Jasper E., Technology Chambers, Irvington St., Boston, Mass.  
Dales, Benton, Univ. of Nebraska, Lincoln, Neb.  
Elliott, E. C., Teachers' College, Columbia Univ., New York City.  
Ferris, W. S., Care of Miami Mining Co., Concord, N. C.  
Fraunfelder, Lewis D., Care of Allegheny Ore & Iron Co., Shenandoah, Va.  
Goodell, Geo. A., 529 N. 123rd St., New York City.  
Hale, Albert C., 352a Hancock St., Brooklyn, N. Y.  
Harms, Armin, Care of Amer. Smelt. & Ref. Co., Monterey, N. L., Mex.  
Heacock, E. A., 110 LaSalle St., Chicago, Ill.  
Hovey, Will C., 143-145 LaSalle St., Chicago, Ill.  
Keller, Cornelius H., Apartado 134, Parral, Chih., Mex.  
Lachman, Arthur, 131 Second St., San Francisco, Cal.  
Lundell, C. E. F., Northwestern Univ. Bldg., Cor. Lake & Dearborn Sts., Chicago, Ill.

MacLeod, (Miss) Grace, Mechanic Arts High School, Springfield, Mass.

Mabery, C. F., 788 Fairmont St., Cleveland, Ohio.

Mallory, J. Halsey, Drawer 69, Columbia, S. C.

Merriam, E. S., Weenderchausée 5, Göttingen, Germany.

Moechel, J. R., Kans. City Chem. Tech. Lab., Kansas City, Mo.

McKenzie, R. Monroe, Parsons College, Fairfield, Iowa.

McMurtrie, Wm., 142 W. 49th St., N. Y. City.

Myers, Ralph E., John Harrison Lab., Univ. of Pa., Philadelphia, Pa.

Nakayama, T., Care Drawn & Co., Canaan Four Corners, N. Y.

Nelson, J. M., Rose Polytechnic Institute, Terre Haute, Ind.

Ober, Julius E., Research Lab., Gen. Electric Co., Schenectady, N. Y.

Overton, A. G., Care Semet Solvay Lab., Ensley, Ala.

Page, Robert W., 123 Halifax St., Raleigh, N. C.

Perley, W. M., 158 Riverside Ave., Medford, Mass.

Reese, Herbert J., Bozeman, Mont.

Rice, W. F., High School, Lyman, Mass.

Rounds, M. B. C., 734 W. 120th St., Chicago, Ill.

Russell, Lee, 11 Green Lane, Worcester, Mass.

Ryland, Garnett, Georgetown, Ky.

Sanders, W. W., Care Jarecki Chem. Co., Sta. P., Cincinnati, O.

Stokes, H. N., Bureau of Standards, Washington, D. C.

Stone, G. C., 71 Broadway, New York City.

Sy, Albert P., Sandy Hook Proving Ground, Fort Hancock, N. J.

Thompson, Firman, New Carlisle, Ohio.

Thompson, John F., School of Metallurgy, Columbia Univ., New York City.

Tingle, Alfred, Imperial Provincial College, Chinanfu, Shantung, China.

Traphagen, F. W., Colo. School of Mines, Golden, Colo.

Wakeman, Alfred J., 819 Madison Ave., New York City.

Whittlesey, Theodore, Northwestern Univ. Bldg., Cor. Lake & Dearborn Sts., Chicago, Ill.

Wiedemann, H. E., Care Nelson Morris & Co., National Stock Yards, Ill.

Wilhelm, Arthur, 1008 Haight St., San Francisco, Cal.

Ziegler, J. Clayton, Naval Proving Grounds, Indian Head, Md.

#### ADDRESSES WANTED.

Pickard, Glen H., formerly 564 W. 118th St., New York City.

Hancock, Thomas, formerly Fruitport, Mich.

Thompson, J. Howard, formerly 372 Atlantic Ave., Boston, Mass.

Welt, Ida, 128 E. 61st St., Milford, Pike Co., Pa.

## Proceedings. COUNCIL.

### MEMBERS ELECTED BETWEEN SEPTEMBER 25 AND OCTOBER 22.

- Adams, Thomas D., 109 De Witt Place, Ithaca, N. Y.  
Bakke, Oliver Mathias, care Oliver Iron Min. Co., Mount Iron, Minn.  
Baxter, Charles Homer, Negaunee, Mich.  
Beckers, W., 40 Howe St., N. Y. City.  
Bishop, W. S., 308 Tioga St., Ithaca, N. Y.  
Cushman, Blin Sill, 109 Elston Place, Ithaca, N. Y.  
Dahlberg, Arnold V., care Oliver Iron Min. Co., Mount Iron, Minn.  
De Veer, Theo., Oxnard, Cal.  
Everett, Ernest T., Jamestown, Cal.  
Everette, Willis E., Tacoma, Wash.  
Fuller, Harry V., care Oliver Iron Min. Co., Mount Iron, Minn.  
Gallup, Frederick L., S. A. E. Lodge, Hill Crest, Ithaca, N. Y.  
Gardner, O. M., A. & M. Coll., West Raleigh, N. C.  
Goodman, Carlton M., care Va. Portland Cement Co., Craigsville, Va.  
Hardy, George D., Belmont Gold Mine, Cordova, Ont.  
Howell, W. L., Appraiser's Office, Custom House, New Orleans, La.  
James, Carton C., Box 65, Palo Alto, Cal.  
Langley, Ralph W., 3435 Morgan St., St. Louis, Mo.  
Morrison, William G., A. & M. Coll., West Raleigh, N. C.  
Oesterle, William F., care Oliver Iron Min. Co., Mount Iron, Minn.  
Palmer, Charles H., care Colo. Smelt. & Ref. Co., Butte, Mont.  
Payne, Clyde A., Ashland, Ore.  
Sands, Ferdinand, Great Falls, Mont.  
Schoellkopf, J. F., 415 Stewart Ave., Ithaca, N. Y.  
Sutzberger, Nathan, Hotel Metropole, Chicago, Ill.  
Talbot, B. Esle, care Gen. Chem. Co., Laurel Hill, L. I., N. Y.  
Williams, William John, 5004 Franklin St., Frankford, Philadelphia, Pa.

### CHANGES OF ADDRESS.

- Annear, J. B., 1028 Regent St., Boulder, Colo.  
Attix, J. C., 873 N. 24th St., Philadelphia, Pa.  
Baltzly, Edwin B., Semet-Solvay Co., Syracuse, N. Y.  
Beistle, Charles P., Sandy Hook, N. J.  
Bennett, Hugh H., Hotel Chattawka, New Bern, N. C.

- Benson, D. H., North Weymouth, Mass.  
 Bird, Herbert S., Royal Baking Powder Co., Kent Ave. and  
 Morton St., Brooklyn, N. Y.  
 Birdsong, John A., Duquesne, Pa.  
 Boggs, Gilbert H., Ga. School of Technology, Atlanta, Ga.  
 Bosart, L. W. Jr., 4615 Montgomery Pike, Norwood, O.  
 Braman, Winifred W., State College, Pa.  
 Chambliss, Hardee, 722 Marcy Ave., Brooklyn, N. Y.  
 Chase, March F., care N. J. Zinc Co., Palmerton, Pa.  
 Colby, Albert Ladd, care International Nickel Co., 43 Exchange Pl., N. Y. City.  
 Cook, A. D., 21 Washington Ave., Warren, O.  
 Dales, Benton, Sta. A, Lincoln, Nebr.  
 Davis, Charles B., care Dr. Francis Wyatt, 39 S. William St.,  
 N. Y. City.  
 DeBlois, W. H., care Gen. Chem. Co., Camden, N. J.  
 Denham, Henry H., 102 W. Beard Ave., Syracuse, N. Y.  
 Earle, Richard B., 20 Read's Block, Cambridge, Mass.  
 Haigh, Leonard D., Box 322, Caro, Mich.  
 Hanson, M., 438 W. Huron St., Chicago, Ill.  
 Haskell, Albert A., West Raleigh, N. C.  
 Hershey, Elam L., R. F. D. No. 2, Lancaster, Pa.  
 Isham, Helen, 14 Morningside Ave., N. Y. City.  
 Jacobson, I., care Reading Foundry Co., Reading, Pa.  
 Jennings, Fred H., 301 Heustis St., Ithaca, N. Y.  
 Jones, J. S., 1329 Louisa St., Berkeley, Cal.  
 Kennedy, Mortimer B., Alpena, Mich.  
 Knapp, R. E., 208 Observatory St., Ann Arbor, Mich.  
 Lenk, Walter S., 110 Cook St., Ithaca, N. Y.  
 Matthews, J. M., 425 S. Broad St., Philadelphia, Pa.  
 McDonnell, M. E., 806 Sixth Ave., Altoona, Pa.  
 McMurtrie, William, 142 W. 49th St., N. Y. City.  
 Mills, J. E., Camden, S. C.  
 Moffatt, Miles R., care Lowell Textile School, Lowell, Mass.  
 Moody, Herbert R., Hobart College, Geneva, N. Y.  
 Norman, G. M., 929 University Ave., Madison, Wis.  
 Odell, J. R., Mass. Inst. Tech., Boston, Mass.  
 Olshausen, B. A., Columbia Univ., N. Y. City.  
 Pickering, O. W., 20 Lenox St., Springfield, Mass.  
 Riederer, Herman S., 251 W. 95th St., N. Y. City.  
 Smith, Arthur G., 2nd and James Sts., Seattle, Wash.  
 Stevenson, Reston, 132 E. Buffalo St., Ithaca, N. Y.  
 Stewart, M. A., 9 Alston St., Somerville, Mass.  
 Sullivan, Eugene C., Chem. Lab., U. S. Geol. Survey, Wash-  
 ington, D. C.  
 Syme, William A., 421 St. Paul St., Baltimore, Md.  
 Trebing, H., 28 Brainard Ave., Cleveland, O.

Warren, Robt. C., care Dr. J. Robt. Moechel, 802 Locust St., Kansas City, Mo.

Weber, R. F., 125 Quarry St., Ithaca, N. Y.

White, Alfred H., 1017 Hill St., Ann Arbor, Mich.

#### DECEASED MEMBERS.

William Ellsworth, of Brooklyn, N. Y., member of the Society since 1898, died in June, 1903.

Arthur W. Walls, of North Woburn, Mass., member of the Society since 1898, died July 7, 1903.

#### HENRY BARKER HILL.

Henry Barker Hill was eminent as a chemist, an administrative officer, and a teacher. He was born in Waltham, Massachusetts, April 27, 1849, the son of the Rev. Thomas Hill, President of Antioch College, and later of Harvard University. After graduating from Harvard College and taking a year of study under A. W. Hofmann, in Berlin, he was appointed Assistant in Chemistry, at Harvard University, in 1870, where he remained as Assistant Professor, Professor, and Director of the Laboratory, until his death, April 6, 1903.

After the publication of two brilliant papers on methyluric acid, in which he described, for the first time, the method of attack, since used with such conspicuous success by Emil Fischer, it was his good fortune to discover furfurol among the waste products of an acetic acid factory, thus securing an unlimited supply of this chemical rarity. He made such a good use of this happy chance that he converted the furfurane group from an unexplored waste into one of the best known of the larger domains of chemistry—an achievement of which any chemist may feel proud. His work on this subject is described in over thirty papers, which show Hill's great qualities as a chemist—his grasp of the subject and power of close and logical reasoning, his uncommon experimental ability, and above all his accuracy and thoroughness. Most chemists are content with the work of their students after testing it at two or three points, but he was never willing to publish until he had repeated the whole of it with his own hands, and, although this diminished the number of his papers, the loss in quantity was more than made up by the finish and authority of his published work.

As Director of the Chemical Laboratory of Harvard University, he was confronted with the problem of forcing the rapidly growing department into an antiquated building, originally planned for forty students, with walls both inside and out of hampering massiveness. Under these discouraging conditions, he contrived adequate laboratories, which were used by seven hundred students, and were enriched by new forms of apparatus, which revolutionize the methods of chemical architecture.

As a teacher, he developed qualitative analysis, too often taught in a purely mechanical way, into one of the best of educational disciplines. His lectures on organic chemistry were models of comprehensiveness and of the preservation of the just relation between the important and the unimportant. Yet with all this devotion to his science he was no narrow specialist, but a man of broad and varied interests and high attainments.

Engrossed in his work and of a retiring disposition, he is known to the chemical world almost exclusively by his researches, so that only a few intimate friends knew his patience, unselfishness, and modesty, his warm, affectionate nature, the fortitude, which never allowed bodily weakness to interfere with his duties, the poise and sanity of his judgment, and above all the entire sincerity, the aggressive honesty, which were the expression of the ruling principle of his life—an almost passionate devotion to truth.

C. LORING JACKSON.

## MEETINGS OF THE SECTIONS.

### NEW YORK SECTION.

The first regular meeting of the Section was held Friday, October 9th, at the Chemists' Club, 108 West 55th Street.

The program for the evening was as follows: "The Volumetric Determination of Zinc," by W. J. Waring; "Nitro-sulphuric Acid and Its Action on Organic Compounds," by C. W. Volney; "The Reduction of Lead from Litharge in Preliminary Assays and the Advantages of an Oxide Slag," by E. H. Miller, E. J. Hall, and M. J. Falk.

H. C. SHERMAN, *Secretary*.

### WASHINGTON SECTION.

The 144th regular meeting was held Thursday, October 8th, in the Assembly Hall of the Cosmos Club.

The program follows : "Second Report on Cement Analyses," by W. F. Hillebrand ; "Precipitation of Zinc by Manganese Peroxide, with Especial Reference to the Volhard Method of Determining Manganese," by Atherton Seidell ; "Solubility of Calcium Sulphate in Dilute Sulphuric Acid," by Frank K. Cameron and J. F. Brezeale.

A. SEIDELL, *Secretary pro tem.*

#### CINCINNATI SECTION.

The 103rd regular meeting of the Section was held in Hanna Hall, University of Cincinnati, Wednesday, October 14th.

The following topics for discussion were presented : "A Method for the Estimation of Chlorides, Bromides, and Iodides," by Stanley Benedict and J. F. Snell ; Reviews, by H. E. Newman.

J. F. SNELL, *Secretary.*

#### CORNELL SECTION.

At the annual meeting held May 28th, the following officers were elected for one year : *President*, W. D. Bancroft ; *Vice-President*, W. R. Orndorff ; *Secretary-Treasurer*, W. C. Geer ; *Executive Committee*, E. S. Shepherd, C. L. Rand, and J. W. Schade.

The first regular meeting of the year was held in Morse Hall, on Tuesday, October 6th.

The program follows : "On Bilirubin, the Red Coloring-matter of the Bile," by J. E. Teeple ; "An Apparatus for the Electrolytic Determination of Metals, Using a Rotating Cathode," by E. S. Shepherd ; "The Resistance of Glass Tubes to Bursting Pressure," by A. W. Browne.

W. C. GEER, *Secretary.*

#### CALIFORNIA SECTION.

The twelfth or annual meeting was held at Café Odeon, in San Francisco, September 12, 1903.

The following officers were elected : J. M. Stillman, *Chairman*; Felix Lengfeld, *Vice-Chairman*; Edmond O'Neill, *Counselor*, and H. E. Miller, *Secretary-Treasurer*. The meeting was preceded by a dinner, served à la carte, and the poor attendance showed conclusively that this is not a popular form of dining. The paper of the evening was by Mr. R. H. Freund, on "The Occurrence of Pentosans in Urine and Their Recognition." After a discussion of the paper, the meeting adjourned.

The thirteenth meeting of this Section was held on Saturday, October 24th, at 8.00 P.M., in Jule's Restaurant, 315 Pine Street, San Francisco, and the paper of the evening was by Professor E. C. Franklin, of Stanford University, on "The Velocity of Ions in Liquid Ammonia Solutions."

HARRY EAST MILLER, *Secretary.*

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#### NOTICE.

In sending the ballots for nominations it should have been stated that the provision of the Constitution, which states that the President and Councilors shall be ineligible to election for a third consecutive term, excludes Messrs. F. A. Gooch and H. L. Wells from re-election. Members who may have voted for one or both of these candidates may still send other names. All ballots must reach the Secretary by November 19th.



## Proceedings. COUNCIL.

MEMBERS ELECTED BETWEEN OCTOBER 22 AND NOVEMBER 19.

Allingham, John, care of L. C. Howell, Box 1026, Johannesburg, So. Africa.

Bailey, Herbert S., 440 W. 15th St., Kansas City, Mo.

Baillio, Gervais, care of Castner Elec. Alk. Co., Niagara Falls, N. Y.

Beardwood, Matthew, 569 Jamestown Ave., Roxboro, Philadelphia, Pa.

Berg, William W., 335 E. 88th St., N. Y. City.

Blackman, Milton J., 1248 Devisadero St., San Francisco, Cal.

Boles, M. M., Columbia Univ., N. Y. City.

Brown, J. Howard, 138 Sandusky St., Jacksonville, Ill.

Brubaker, Howard W., Room 15, House P., U. of Pa. Dormitories, Philadelphia, Pa.

Chamberlin, George M., Jr., 2136 Sixth St., Bay City, Mich.

Coblentz, Lambert, 122 Broderick St., San Francisco, Cal.

Craine, Charles R., 42 Pooley Place, Buffalo, N. Y.

Dempwolf, Charles H., Jr., York, Pa.

Dimpfel, G. W., P. O. Box 98, Scranton, Pa.

Duncan, William Wheeler, 406 Massachusetts Ave., Boston, Mass.

Ebersole, Morris R., 222 Lake St., Chicago, Ill.

Eckstein, Oskar, Tufts College, Mass.

Eilers, Heye E., Room 26, Chrampton Hall, Jacksonville, Ill.

Emerson, Herbert W., Univ. of Kans., Lawrence, Kans.

Formico, Otto, 436 W. 45th St., N. Y. City.

Haddock, Isaac T., Tiverton, R. I.

Hahn, Albert W., 245 W. 130th St., N. Y. City.

Hanson, Herman H., Orono, Me.

Henry, David Hill, Clemson College, S. C.

Hoffman, Alfred, 217 Hewes St., Brooklyn, N. Y.

Hutchins, E. B., Madison, Wis.

Joyce, Clarence M., care of Arlington Co., Arlington, N. J.

Lowe, Charles Otho, 261 Clerk St., Jersey City, N. J.

Merrihew, L. H., 74 W. Main St., Chicago Heights, Ill.

- Neugass, Solomon, 257 W. 132d St., N. Y. City.  
 Philbrick, (Miss) Annie, Wellesley College, Wellesley, Mass.  
 Pinkerton, Thos. C., Beacon Chambers, Boston, Mass.  
 Pulsifer, H. B., Durham, N. H.  
 Schaller, Waldemar T., U. S. Geol. Survey, Washington, D. C.  
 Schwarz, Herbert F., 290 E. Merrimack St., Lowell, Mass.  
 Scudder, Harold H., Durham, N. H.  
 Smith, Melvin M., Dover, N. H.  
 Smith, Ralph Ogden, Univ. of Pa. Dormitories, Philadelphia, Pa.  
 Stillwell, Albert G., 36 Gold St., N. Y. City.  
 Taylor, Jackson Brooks, Newburgh, N. Y.  
 Twitmyer, Joseph C., care of Larkin Soap Co., Buffalo, N. Y.  
 Wallbridge, William K., 29 E. 22d St., N. Y. City.  
 Wemple, Leland E., 1260 W. College Ave., Jacksonville, Ill.  
 White, Frederick S., 70 Pierrepont St., Brooklyn, N. Y.  
 Woodley, George F., 37 Norfolk Ave., Roxbury, Mass.

## CHANGES OF ADDRESS.

- Abbott, Francis L., Donora, Pa.  
 Acree, S. F., Kurfürster Strasse 48, Berlin, Germany.  
 Allen, Chas R., New Bedford, Mass.  
 Arnold, L. L., 5527 Columbo St., Pittsburg, Pa.  
 Baxter, Wm. T., Eastern Laboratory, P. O. Box 257, Chester, Pa.  
 Beck, Oscar C., care of Henry R. Worthington, Elizabethport, N. J.  
 Berry, G. M., 814 Franklin St., Edgewood Park, Pa.  
 Berkeley, W. N., Box 466, San Juan, Puerto Rico.  
 Bowey, J., Jr., Coropolis, Pa.  
 Cady, W. B., care of Peninsular Portland Cement Co., Cement City, Mich.  
 Clark, Friend E., Pennsylvania State College, State College, Pa.  
 Clevenger, G. H., Rapid City, S. D.  
 Colby, Albert Ladd, care of International Nickel Co., 43 Exchange Place, N. Y. City.  
 Colley, B. T., care of Am. S. & R. Co., Aguas Calientes, Mex.  
 Dickie, Albert E., N. J. Military Academy, Freehold, N. J.  
 Ebaugh, Clarence W., 1105 E. 2 South St., Salt Lake City, Utah.

- Falk, Kaufman G., Gailerstrasse 14, Strasburg i/Els., Germany.  
Fisher, Fred., Marlboro, Mich.  
Foster, J. Preston, Central Tinguaro, Perico, Cuba.  
Fraunfelder, L. D., 231 Cattell St., Easton, Pa.  
Grosse, S. P., Ferro Carrill Mexicana Central, Teloloapan, Guerrero, Mexico.  
Haff, Max M., 77 Gloucester St., Ottawa, Canada.  
Haas, Herbert, Supt. Reduct. Wks. Great Western Gold Co., Redding, Cal.  
Hanson, Martin, 438 W. Huron St., Chicago, Ill.  
Holm, M. L., care of N. W. Univ. Med. School, 2421 Dearborn St., Chicago, Ill.  
Kennedy, Mortimer B., 556 State St., Ann Arbor, Mich.  
Landis, W. S., 211 S. New St., Bethlehem, Pa.  
Langmuir, Irving, Weender Ch., 5, Göttingen, Germany.  
Law, Leroy M., 629 8th St., N. E., Washington, D. C.  
Lee, Waldemar, 4620 Wayne St., Philadelphia, Pa.  
Loeb, Morris, 273 Madison Ave., N. Y. City.  
Lyon, A. C., 404 Matthews St., Columbia, Mo.  
Madison, Herbert F., Leetonia, O.  
Mather, Stephen A., Lakeside, Ill.  
Miller, Stephen C., 22 N. Y. Ave., N. E., Washington, D. C.  
Muller, Robt., Rush, Tex.  
Murray, C. B., care of St. Louis Plate Glass Co., Valley Park, Mo.  
Nelson, John M., Rose Polytechnic Institute, Terre Haute, Ind.  
Nish, John C., 159 Pearl St., Boston, Mass.  
Parmelee, H. C., 1755 Arapahoe St., Denver, Colo.  
Perry, Chas. M., 4 Catalpa Road, Providence, R. I.  
Petraeus, Carl V., St. Louis Smelting and Ref. Co., St. Louis, Mo.  
Philipp, Herbert, 92 Gordon St., Perth Amboy, N. J.  
Pickering, O. W., 20 Lennox St., Springfield, Mass.  
Pond, F. J., 86 Valley Road, Montclair, N. J.  
Powers, Irwin La Verne, 9 Hanover St., Lynn, Mass.  
Ross, Samuel, Chem. Lab., Cudahy Pack. Co., So. Omaha, Neb.  
Scherubel, E. F., 686 57th St., Hyde Park, Chicago, Ill.  
Schoonmaker, H., 734 W. 9th St., Cincinnati, O.  
Schuyler, Erwin, 909 W. 8th St., Erie, Erie Co., Pa.  
Sellers, J. F., Macon, Ga.

Sharwood, W. J., 2119 Durans Ave., Berkeley, Cal.  
Starke, Eric A., 2655 Dwight Way, Berkeley, Cal.  
Taylor, M. A., Leetonia, O.  
Thompson, Firman, Sugar Expt. Sta., Honolulu, Hawaii.  
Thurlow, Nathaniel, 226 E. Frederick St., Lancaster, Pa.  
Tibbals, C. A., Jr., 604 Francis St., Madison, Wis.  
Torrey, Henry A., Boylston Hall, Cambridge, Mass.  
Turrentine, J. W., Lafayette College, Easton, Pa.  
Walker, Percy H., P. O. Box 231, Scranton, Pa.  
Wallenstein, Florian, Berlin S. O., Rungestr 20.  
Warville, Francis G., 5711 Madison Ave., Hyde Park, Chicago,

III.

Weed, Henry T., 408 Third St., Brooklyn, N. Y.  
Welt, Ida, 73 W. 83d St., N. Y. City.  
White, Alfred H., 1017 Hill St., Ann Arbor, Mich.  
Wolcott, Clifford H., 602 Van Buren St., Chicago, Ill.  
Woods, Fred L., 113 N. Ingallo St., Ann Arbor, Mich.  
Worden, Edward C., Clark Thread Co., Newark, N. J.

ADDRESSES WANTED.

Breed, Charles H., formerly U. S. Steel Co., W. Everett, Mass.  
Browne, Lyman M., formerly 120 Huntington Ave., Boston,  
Mass.  
Coover, Winifred F., formerly 1456 Hunter St., Columbus, O.  
Du Pont, Francis G., formerly Montchanin, N. J.  
Egloffstein, C. M., formerly 58 Garden St., Boston, Mass.  
Franklin, Arthur I., formerly Pullman, Chicago, Ill.  
Hovey, Will C., formerly 145 La Salle St., Chicago, Ill.  
Johnston, Oscar P., formerly 123 Linn St., Ithaca, N. Y.  
Phillips, W. D., formerly 128 Pearl St., N. Y. City.  
Ryland, Garnet, formerly Georgetown College, Washington,  
D. C.  
Sweeton, (Miss) Agnes G., formerly Sage Hall, Ithaca, N. Y.  
Thompson, Howard J., formerly 372 Atlantic Ave., Boston,  
Mass.  
Turner, B. B., formerly, 103 Linn St., Ithaca, N. Y.  
Urner, Frank A., formerly 221 Eddy St., Ithaca, N. Y.

DECEASED MEMBER.

Dr. Henry Carrington Bolton, of Washington, D. C., member of the Society since 1891, died November 19, 1903.

CONGRESS OF ARTS AND SCIENCE.

Professor Simon Newcomb, chairman of the Organizing Committee for the Congress of Arts and Science at St. Louis, has requested the Council to suggest names of the most eligible chemists for the places of chairmen, secretaries and speakers in the department of chemistry, and its four sections. It is intended that two addresses shall pertain to the whole department of chemistry, the one reviewing its progress during the last century, and the other setting forth its fundamental conceptions and methods. In each of the four sections, two addresses are expected. One of these will be given by the following foreign chemists: Professor Mendeléef, Fittig, van't Hoff and Kossel, of whom all except Professor Mendeléeff have given their acceptance. Four American speakers in these same fields are desired. In each of the four sections one address is expected on the relations of the particular section to the other sciences, and the other on the problems of to-day.

In accordance with this request, it has been moved that President Long be directed to suggest names to Professor Newcomb on the basis of a vote by the Council, nominating chemists for the positions in question.

MEETINGS OF THE SECTIONS.

CORNELL SECTION.

The November meeting of the Section was held in Morse Hall on Tuesday evening, November 3d. The Section was addressed by Professor G. W. Cavanaugh on "Some Applications of Chemistry in Modern Agriculture." Mr. I. Baum reported on his investigations of electrolytic copper refining.

W. C. GEER, *Secretary*.

CINCINNATI SECTION.

The 104th regular meeting of the Section was held at the Ohio

Mechanics Institute, Sixth and Vine Sts., Wednesday, November 18th, at 8 o'clock P.M.

The following topics for discussion were presented: "The Assay of Tobacco and Nicotine-Solutions," by S. Waldbott. Reviews, by H. E. Newman and O. W. Martin.

J. F. SNELL, *Secretary.*

#### NEBRASKA SECTION.

The 33d regular meeting of the Nebraska Section was held in the Chemical Laboratory of the University of Nebraska, Saturday, November 14th. Program: "The Rare Earths and the Methods of Their Separation," by Dr. Benton Dales.

BENTON DALES, *Acting Secretary.*

#### WASHINGTON SECTION.

The 145th regular meeting was held Thursday, November 12th, in the Assembly Hall of the Cosmos Club, 1520 H St., N. W.

Program: "European Notes," by Prof. F. W. Clarke; "Solubility of Calcium Sulphate in Dilute Sulphuric Acid," by Frank K. Cameron and J. F. Breazeale.

A. SEIDELL, *Secretary pro tem.*

#### PITTSBURG SECTION.

The regular monthly meeting was held with the Chemical Section of the Engineers' Society of Western Pennsylvania, at 410 Penn Ave., Thursday evening, November 19th.

Papers were presented by Mr. Harry E. Mali, on "The Jellies of Pittsburg," and by Mr. J. O. Handy, on "The Chemistry of Water Purification."

GEO. P. MAURY, *Secretary.*







